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PB-279 010

International Conference on Oxidants, 1976
Analysis of Evidence and Viewpoints. Part III
The Issue of Stratospheric Ozone Intrusion

State Univ. of New York at Albany

Prepared for

Environmental Sciences Research Lab., Research Triangle Park, NC

Dec 77

EPA-600/3-77-115
December 1977

PB 279 010

Ecological Research Series

INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 - ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part III. The Issue of Stratospheric Ozone Intrusion

Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/3-77-115

2.

3. RECIPIENT'S ACCESSION NO.
PB279010

4. TITLE AND SUBTITLE
INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 -
ANALYSIS OF EVIDENCE AND VIEWPOINTS
Part III. The Issue of Stratospheric Ozone Intrusion

5. REPORT DATE
December 1977

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
1. V.A. Mohnen
2. E.R. Reiter

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
1. State Univ. of N.Y., Albany, NY
2. Colorado St. Univ., Fort Collins, CO

10. PROGRAM ELEMENT NO.
1AA603 AJ-13 (FY-76)

11. CONTRACT/GRANT NO.
1. DA-7-1936A
2. DA-7-1305J

12. SPONSORING AGENCY NAME AND ADDRESS
Environmental Sciences Research Laboratory - RTP, NC
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

13. TYPE OF REPORT AND PERIOD COVERED
Final

14. SPONSORING AGENCY CODE
EPA/600/09

15. SUPPLEMENTARY NOTES
Partially funded by the Office of Air Quality Planning and Standards.

16. ABSTRACT

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In Part III V.A. Mohnen and E.R. Reiter discuss the issue of stratospheric ozone intrusion, i.e., whether ozone of stratospheric origin contributes significantly to ground-level ozone buildup. The literature on the subject of ozone intrusion is discussed and suggestions for further research to resolve some of the questions raised are made.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
* Air pollution * Ozone * Stratosphere		13B 07B 04A

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
145

22. PRICE
PCA07-A01

EPA Form 2220-1 (9-73)

EPA-600/3-77-115
December 1977

INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 — ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part III. The Issue of Stratospheric Ozone Intrusion

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5 day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a followup review/analysis effort. The followup effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

In Part III V.A. Mohnen and E.R. Reiter discuss the issue of stratospheric ozone intrusion, i.e., whether ozone of stratospheric origin contributes significantly to ground-level ozone buildup. The literature on the subject of ozone intrusion is discussed and suggestions for further research to resolve some of the questions raised are made.

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This part contains the following

CONTENTS

ABSTRACT iii

FIGURES vi

TABLES. x

INTRODUCTION 1
B. Dimitriades and A.P. Altshuller

THE ISSUE OF STRATOSPHERIC OZONE INTRUSION 3
B. Dimitriades and A.P. Altshuller

REVIEW AND ANALYSIS. 7
V.A. Mohnen

- Introduction. 7
- Ozone Intrusion into the Troposphere and Subsequent Downward Transport to the Sink Region near and at the Earth's Surface. 14
- Measurements Focusing on Stratospheric-Tropošperic Exchange Processes 20
- Measurements of the Representative Ground-Level Ozone Concentrations 33
- Summary 63
- Acknowledgements. 64
- Comments by Elmar Reiter. 64

REVIEW AND ANALYSIS. 67
E.R. Reiter

- Abstract 67
- Introduction. 67
- The Stratospheric Reservoir 68
- Stratospheric-Tropospheric. 73
- The Life History of Stratospheric Intrusion Episodes. 99
- Conflicting Evidence from Direct Ozone Measurements 103
- Conclusion. 115
- Suggestions for Future Research 115
- Comments by Volker Mohnen 118

REFERENCES 125

FIGURES

REVIEW AND ANALYSIS - V.A. Mohnen

Number Page

1 Tentative model of ozone fluxes produced by the general circulation. 8

2 Comparison between year-to-year variations in different layers and of the total amount over Switzerland 1967-1972. 9

3 Variation of integrated vertical ozone column with season at tropical, temperate, and polar zones. 10

4 North American ozonesonde network. 11

5 Two-year average transport of ozone by transient eddies from December to May 1962-1964. Transient eddy ozone transport, 1962-1964 12

6 Average ozone mass mixing ratio distribution for spring 1963-1964. 14

7 Time series of comparison between cyclone indes and shorter period fallout fluctuations. 17

8 Average tropopause heights for the period 1946-1956 at Swan Island (17°N), Phoenix (33°N), North Platte (41°N), and International Falls (49°N) 19

9 Vertical profiles of ozone mixing ratio (thin line) and potential vorticity (heavy line) derived from Figure 12 for Bedford, Mass., and Tallahassee, Fla., 1200 GMT 24 April 1963. 21

10 Potential vorticity (contoured at intervals of 100 x 10^{-10}cm sec (°K gm^{-1}) computed from Figure 2 and β activity of SR^{90} (dpm/KSCF). 22

11 Vertical cross-section of potential vorticity in units of 10^{-10} cm sec deg g^{-1} 23

12 Trajectories on the 300°K isentropic surface 24

Number Page

13 Heavy line is monthly mean variation of GASP ozone at 11-12 km, 36-42°N from March, 1975, through March, 1976 28

14 Solid lines are "zonal" means of ozone (ppbv) at 10° latitude belts for combined March data (1975 and 1976) .

15 Vertical profiles of the global vertical ozone transport . . 32

16 Annual variation of monthly average values of daily maximum ozone concentration at various places. 37

17 Probability of the occurrence of the daily maximum of ozone near the ground over hourly intervals. 41

18 Correlation of mean ozone values measured within the Prandtl layer (2.5 - 10 m) with ozone concentration of the layer between 97.5 and 105 m 42

19 Monthly means of tropospheric ozone, derived from near surface registrations of project TROZ. 43

20 Variation of ozone mixing ratio with latitude for March and May. 44

21 Mean residence time of ozone in the troposphere assuming destruction at the surface to be the only sink 47

22 Frequency distribution of ozone concentration at Whiteface Mt. during 1974. 51

23 Ozone trend and potential temperature trend (850 mb) at Whiteface Mt. 53

24 Isentropic analysis and ozone concentration - Whiteface Mt.- July 1975. 54

25 Correlation of tropospheric ozone mixing ratio for a day T with mixing ratio for day T-1. 58

26 Correlation of tropospheric ozone mixing ratio for day T with mixing ratio for T-2. 59

27 Secular variation of tropospheric ozone concentration over North America (μg/g) 61

28 Mean, monthly ozone mixing ratios obtained in the upper troposphere by participating GASP airliners. 62

FIGURES

REVIEW AND ANALYSIS - E.R. Reiter

Number		Page
1	Monthly mean total ozone amounts at Arosa, Switzerland (46.5°N, 9.4°E).	69
2	Comparison of the smoothed sunspot number with the total-ozone variation in regions with the longest records and most stations.	70
3	Temporal variation in total ozone in West Europe by season .	71
4	Worldwide total ozone as a function of season and latitude .	72
5	Stratospheric inventory of Sr^{90}.	75
6	Pole-to-pole cross-section of vertical ozone distribution in nb (1 nb = 0.1 N/m^2).	77
7	Vertical cross-section of potential vorticity (10^{-10} cm sec deg/g), Zr^{95} activities (dpm/scf), and ozone mixing ratios (10^{-7} g/g).	78
8	Mean meridional circulation (mass flow in units of 10^{12} g sec^{-1}) for the four seasons.	80
9	Schematic three-dimensional view of mass flow from stratosphere to troposphere near a jet stream.	85
10	Time series of comparison between cyclone index, C, and shorter period fallout fluctuations.	87
11	Daily values of energy by mode and for the total of available potential plus kinetic energy from July 1967 through June 1968.	88
12	Mean ozone distribution for March-April (solid lines, slanting numbers, µg/g) and Sr^{90} distribution for May-August 1963 (dashed lines, vertical numbers, dpm/1000 SCF)	90
13	Sr^{90}/O_3 ratios as a function of time	91
14	Mean fallout, January-June 1963, pCi/m^3.	94
15	Number of days with fallout $\geq$ 10 pCi/m^3, 1963.	95
16	Maximum 24-hour fallout 1963, pCi/m^3	96

Number		Page
17	Percent frequency distribution of ozone concentrations (ppb) observed at Zugspitze, Germany, from August 1973 to October 1975	97
17a	Mean seasonal variation of tropospheric ozone from airplane measurements for the areas 0° - 25°S and 0° - 25°N . . .	98
18	Trajectories on the 300°K isentropic surface	101
19	Difference between maximum hourly ozone concentrations (ppb) and daily mean concentrations as a function of daily mean concentrations, observed at Zugspitze (3000 m above MSL) between August 1973 and February 1976	105
20	100-mb map, 7 January 1975, 00 GMT	107
21	Average monthly ozone concentrations recorded at summit of Mount Whiteface.	108
22	Ozone concentrations at Whiteface and Pack Forest from August 6, 1973 to August 17, 1973	109
23	Hourly ozone averages at Whiteface, Pack Forest, and Glens Fall sites for July, 1973.	109
24	Comparison of ozone concentration at Whiteface site with that at Utsayantha and Syracuse sites for the first 17 days of August, 1973.	110
25	The mean maximum mixing depth for January and July	112
26	Measurements of ozone and other meteorological problems at Hohenpeissenberg (977 MSL), Germany.	113

TABLES

REVIEW AND ANALYSIS - V.A. Mohnen

Number Page

1 Summary of GASP Data 26

2 Ozone Mixing Ratio 30

3 List of Stations of Project TROZ 39

4 Average Mean a_1, Amplitude a_2 and Phase a_3, of Annual Wave and Their Mean Statistical Error 45

5 Calculation of Global Sink 48

6 Classification of Critical Ozonagrams by Vertical Distributions ($> 0.10\ \mu g \cdot g^{-1}$ below 500 mb). 56

REVIEW AND ANALYSIS - E.R. Reiter

Number Page

1 Annual Mass Flux from Stratosphere, in Percent of Mass of One Hemispheric Stratosphere 73

2 Mass Flux from Stratosphere to Troposphere Accomplished by Hadley Cell Circulation 76

3 Percentage Contribution of Particular Nuclides in Total Monthly Radioactive Debris Measured in Rainfall at Westwood, New Jersey 92

4 Decrease of P Along 12-Hour Trajectory Segments. 100

5 Hourly Ozone Concentrations (ppb), Zugspitze (Germany) on January 8 and 9, 1975 106

ACKNOWLEDGMENTS

These contracts were jointly funded by the Office of Research and Development (Environmental Sciences Research Laboratory) and the Office of Air Quality Planning and Standards.

The assistance of the technical editorial staff of Northrop Services, Inc. (under contract 68-02-2566) in preparing these reports is gratefully acknowledged.

INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted out by EPA to non-EPA, non-industry scientists with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of stratospheric ozone intrusion. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow, along with the experts' comments on each other's reports.

THE ISSUE OF STRATOSPHERIC OZONE INTRUSION

Basil Dimitriades and A. Paul Altshuller

In a broad sense, the question at issue here is whether ozone of stratospheric origin contributes significantly to the ozone problems observed in urban and rural areas. Aside from the possibility that stratospheric-tropospheric exchange contributes directly and significantly to ground-level ozone buildup, stratospheric ozone has also been proposed to have a "reaction-trigger" function that accelerates and enhances photochemical oxidant formation from hydrocarbon-NO_x precursors. The stratospheric ozone intrusion question is part of the broader question regarding the magnitude and extent of the ozone problem caused by natural causes, which in turn is a part of the issue of achievability of the National Air Quality Standard for Oxidants (NAQS-O_x). To further explain the interest in the stratospheric ozone question, it should be clarified and stressed here that this question, in fact the entire issue of achievability of the NAQS-O_x, has no bearing whatever upon the justification of the NAQS-O_x; such justification is based strictly on health effects considerations. The stratospheric ozone question needs to be answered only for the purpose of more accurately estimating the benefits to be derived from anthropogenic emission reduction.

Evidence interpreted to show accumulation of stratospheric ozone within the troposphere varies widely in type and degree of directness. Thus, high levels of ozone were measured in the upper troposphere near tropopause discontinuity points (2), evidence that attests to stratospheric origin most directly. On the other extreme, ground-level oxidant buildup in some instances was attributed by investigators to stratospheric intrusion only because these investigators did not have or would not accept any other explanations (3). Overall, direct, unequivocal evidence on the impact of stratospheric ozone intrusion upon tropospheric air quality is lacking, and for this

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reason it may be expected that the viewpoints and interpretations of evidence expressed to date reflect to some — perhaps substantial — degree a subjective judgment.

At present, a realistic assessment would suggest that the extent (by area), intensity (by concentration), and frequency of occurrence of stratospheric ozone buildup at ground level, all vary widely so that single answers and answers to all of the questions that constitute the issue cannot be given. It would, therefore, be more productive to define and offer as the subject of this review only those that are most relevant to the oxidant control strategy issue and receive substantial research attention. These questions are proposed here to be as follows:

1. Accepting that intensive stratosphere-troposphere exchanges do occur at tropopause discontinuity points, what is the extent, frequency, duration, and spatial/temporal predictability of such occurrences?

The terms "extent" and "spatial" here refer to areas at high altitudes, that is, near the tropopause, not at ground level. While quantitative answers are not expected, at least, a judgment should be made whether such exchanges are sporadic, unpredictable incidents causing local ozone accumulations or are significantly extensive and predictable. Main interest, of course, is in occurrences within the U.S.

2. Accepting that localized high concentrations of stratospheric ozone can occur in the *upper* troposphere, what fraction of such ozone is expected to reach ground level
    (a) under meteorological conditions most conducive to downward transport, and
    (b) under meteorological conditions most conducive to photochemical oxidant formation?

The questions asked here, in essence, are again whether or not stratospheric ozone excursions *to ground level* are sporadic, unpredictable incidents causing only local, short-lived (e.g., a few hours) ozone accumulations, and whether or not such excursions are likely to occur during smog episode periods.

The question concerning the possible "reaction-trigger" function of stratospheric ozone is not raised here because, thus far at least, it has been a subject of speculation only; no relevant evidence apparently exists, except for a few as yet unreported smog chamber experiments. Nevertheless, comments from the reviewers on this question are welcome.

REVIEW AND ANALYSIS

Volker A. Mohnen

INTRODUCTION

The fundamental aspects of the "classical hypothesis of the ozone cycle" are:

- Photochemical production in the stratosphere, mainly at low latitudes (ozone source region, above 20-km altitude);
- Poleward flux through stratospheric general circulation;
- Intrusion into the troposphere through stratospheric-tropospheric exchange processes;
- Mixing in the troposphere;
- Ozone destruction within the planetary boundary layer and at the earth's surface (sink region).

These mechanisms are shown diagrammatically in Figure 1 (4). Processes 1 and 2 are not the subject of this limited literature assessment.

A reasonable hypothesis of the three-dimensional ozone distribution in the stratosphere and its variation with time presently exists. With a few exceptions, this knowledge is not yet accurate enough to definitely describe ozone fluxes, and the flux-producing mechanisms. Hence, we cannot accurately predict the total ozone* content (mainly stratospheric ozone) as a function of latitude and season.

---

* The total ozone content of the atmosphere over a fixed point is given as the thickness of the pure ozone layer that would be obtained if all ozone in a 1 cm^2 vertical column were concentrated at normal temperature and pressure (NTP). It is usually expressed in units of one thousandth (10^{-3}) of a cm and is equal to 2.687×10^{16} molecules/cm^2 column. This unit is also called the Dobson unit (DU). Vertical ozone distribution data may be present in terms of ozone density ρ_3 measured in $\mu g/m^3$. The conversions to other units and ozone parameters are as follows:

$\text{molecules}\cdot m^{-3} = 1.255 \times 10^{16} \times \rho_3\ (\mu g\cdot m^{-3})$

$\text{partial pressure in nanobars} = 1.732 \times 10^{-3} \times T(°K) \times \rho_3\ (\mu g\cdot m^{-3})$

$\text{mixing ratio in } \mu g\cdot g^{-1} = [2.871 \times 10^{-3} \times \rho_3\ (\mu g\cdot m^{-3}) \times T(°K)]/P(mb)$

$m\ \text{atm} - \text{cm}\ km^{-1} = 4.67 \times 10^{-2} \times \rho_3\ (\mu g\cdot m^{-3})$

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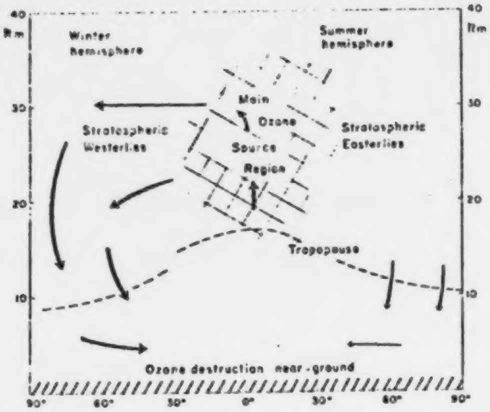

40
km
Winter hemisphere
Summer hemisphere
30
Main Ozone Source Region
Stratospheric Westerlies
Stratospheric Easterlies
20
Tropopause
10
Ozone destruction near-ground
90°
60°
30°
0°
30°
60°
90°

Figure 1. Tentative model of ozone fluxes produced by the general circulation.

Source: "The Ozone Distribution in the Atmosphere," H.U. Dutsch. Can. J. Chem., 52, 1974.

The best available long-term record of total ozone (beginning in 1933) is from Arosa, Switzerland 46.5°N, 9.4°E (see Figure 2). Of particular interest in Figure 2 is the total ozone amount in the 125-250 mb layer since this layer constitutes a potential "ozone reservoir" for the troposphere. The systematic natural variation of total ozone with season and with latitude (compiled mainly from ozonesonde data) is given in Figure 3. The seasonal variation is clearly dominated by transport processes leading to the late winter-spring maximum. Results from the ozonesonde network, established by the Air Force Cambridge Research Laboratories in January 1963 (see Figure 4), indicate that the northward transport of ozone across middle latitudes over North America occurs predominately in the lower stratosphere and just above the tropopause. The average flux strength observed in the summer and fall seasons is less than one-third of the average winter and spring transport. Figure 5 shows the 2-year average values calculated for the winter and spring seasons for three stations near 40°N. The indicated eddy flux diminishes sharply above 16 km to rather small values. Also shown in Figure 5 is the 2-year average temporal eddy flux for the winter and summer half years. The overall flux strength is much weaker during the less vigorous and less disturbed circulation regime in the summer and fall seasons. If the indicated transports are indeed representative of the average hemispheric flux, the total northward ozone transport across middle latitudes would be 1.4 x 10^9 tons for the cold half year and 0.4 x 10^9 tons for the warm half year (5).

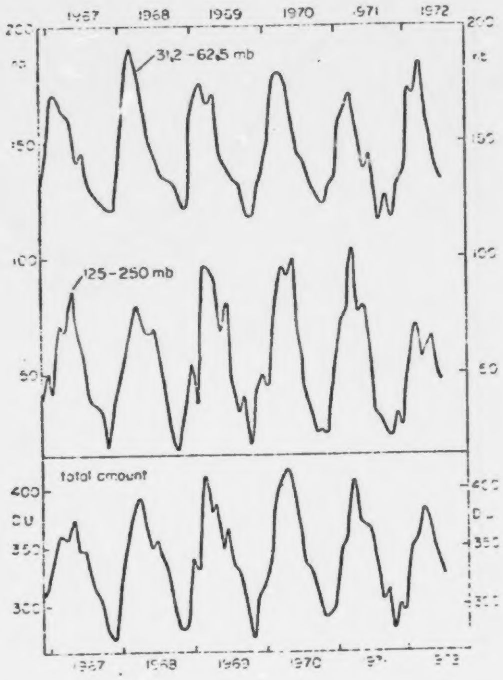


Figure 2. Comparison between year-to-year variations in different layers and of the total amount over Switzerland 1967-1972. (From Ref. 14)

Source: "The Ozone Distribution in the Atmosphere," H.U. Dutsch. Can J. Chem., 52, 1974.

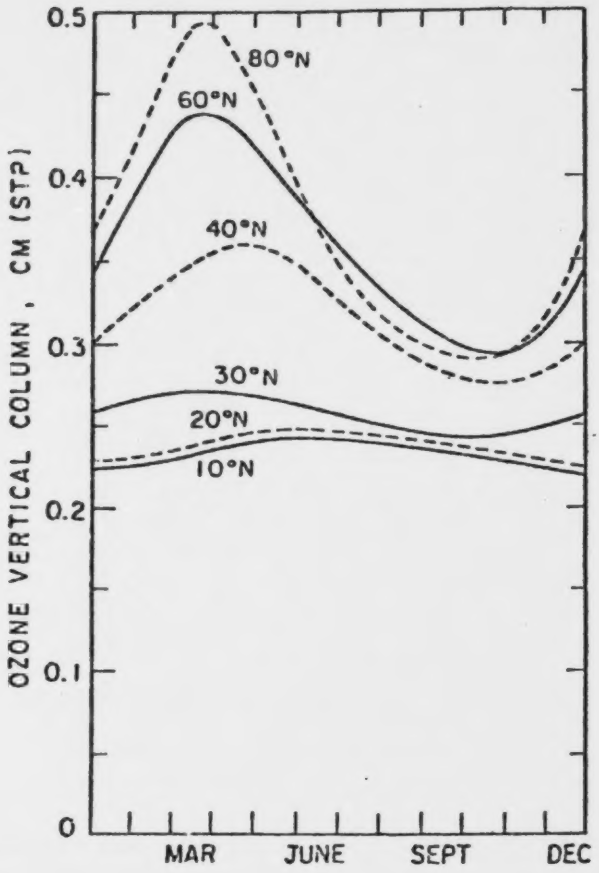
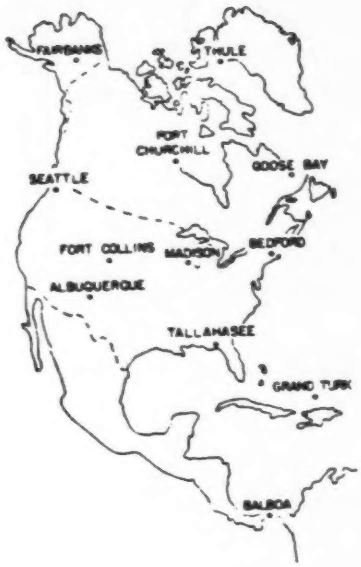


Figure 3. Variation of integrated vertical ozone column with season at tropical, temperate, and polar zones.

Source: Environmental Impact of Stratospheric Flight. Biological and Climatic Effects of Aircraft Emissions in the Stratosphere. National Academy of Sciences, Washington, D.C., 1975.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GRAND TURK
BALBOA

Figure 4. North American ozonesonde network.

Source: "Ozone and atmospheric transport processes," W.S. Hering. Tellus XVIII (1966), 2.

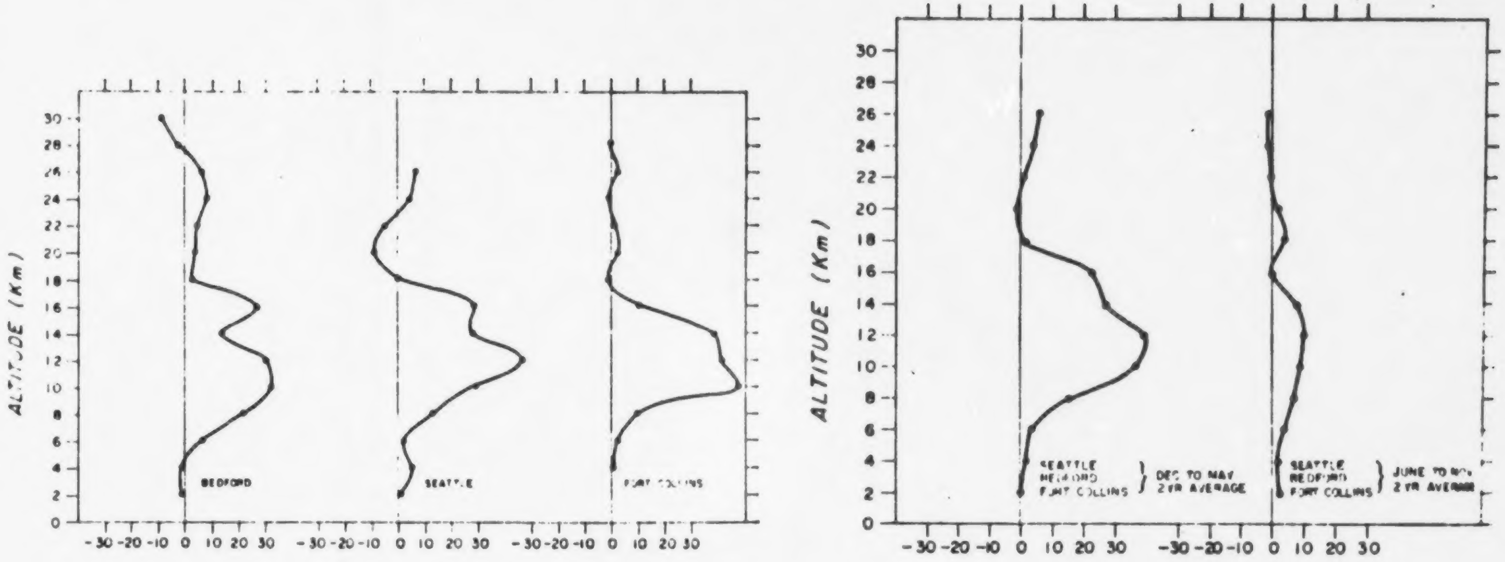


Figure 5. Two-year average transport of ozone by transient eddies from December to May 1962-1964. Values are in 10^{-9}gm $sec^{-1}cm^{-2}$. Transient eddy ozone transport, 1962-1964, in 10^{-9} gm $sec^{-1}cm^{-2}$.

Source: "Ozone and atmospheric transport processes," W.S. Hering. Tellus XVIII (1966), 2.

The *average* seasonal distribution of ozone mixing ratio along a cross-section extending from the Canal Zone, Panama, to Thule, Greenland, is shown in Figure 6 as derived from a total of 421 ozonesonde ascents obtained from the AFCRL in 1963 and 1964. The average tropospheric ozone amount is around 0.05 μg/g with a small but *significant maximum* at 30° to 40°N. Another important result derived from the AFCRL ozonesonde network is that the potential vorticity* computed from monthly-mean cross-sections is positively correlated throughout the lower stratosphere with the bimonthly mean values of ozone mixing ratio (6).

These general conclusions can be drawn from this rather limited data:

- In the latitude range 40-50°N (i.e., the area covering the U.S. continent), the northward transport of ozone occurs mainly in the lower part of the stratosphere.
- The average flux strength for "winter-spring" is about three times that for "summer-fall" in the latitude range 40-50°N.
- The average meridional flux strength and the depth of the total ozone column exhibit a sinusoidal behavior during the year. The mean and the amplitude of both are latitude dependent.
- Potential vorticity and ozone concentration exhibit a positive correlation in the stratosphere.

---

* Potential vorticity (P_Θ) is a quasi-conservative scalar whose large values are generated in the middle stratosphere by diabatic radiative processes. $P_\Theta = -Q_Z \frac{\delta\Theta}{\delta P}$ [$\mathrm{cm \cdot s \cdot deg \cdot g^{-1}}$] with Q_Z the vertical component of absolute vorticity; Θ the potential temperature; and P the pressure. Potential vorticity is conserved in adiabatic flow. Values of $P \geq +100 \times 10^{-10}\ \mathrm{cm \cdot s \cdot deg \cdot g^{-1}}$ are characteristic of stratospheric air. Potential vorticity is destroyed in the troposphere by diabatic mixing, overturning, and frictional dissipation at the ground.

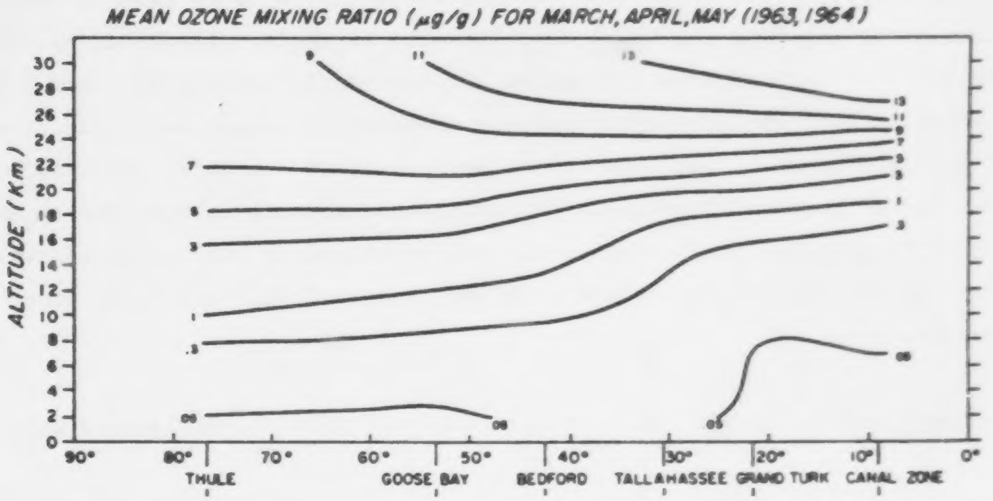


Figure 6. Average ozone mass mixing ratio distribution for spring 1963-1964. Values are in µg/g or ppm.

Source: "Ozone and atmospheric transport processes," W.S. Hering. Tellus XVIII (1966), 2.

OZONE INTRUSION INTO THE TROPOSPHERE AND SUBSEQUENT DOWNWARD TRANSPORT TO THE SINK REGION NEAR AND AT THE EARTH'S SURFACE

The third, fourth, and fifth processes, in the initial hypothesis, will now be discussed in some detail. Existing literature references to these processes can be classified into two main categories:

- Those describing measurements of the stratospheric-tropospheric exchange processes with emphasis on identifying and quantifying these processes. Stratosphere to troposphere ozone fluxes are then calculated from these measured values.
- Measurements of the representative ground-level ozone concentration ("tropospheric background"), its diurnal, seasonal, and secular variation, and of the ozone destruction rates near and at the earth's surface. Stratospheric-tropospheric ozone fluxes can then be calculated from the rates of change in concentration.

Since ozone transport is achieved by means of mass transfer between stratosphere and troposphere, it is imperative to have some quantitative mass transfer estimates in conjunction with the ozone mixing ratio for these stratospheric air mass intrusions. The following processes are responsible for stratospheric-tropospheric mass exchange (7):

A - Large-scale eddy transports, mainly in the jet-stream region;

B - Seasonal adjustments in the height of the mean tropopause level;

C - Mesoscale and small-scale eddy transport across the tropopause;

D - Organized large-scale quasi-horizontal and vertical motions expressed by the mean meridional circulation.

Referring to process A, transport occurs when the boundary between the stratosphere and the troposphere deforms (in this case the tropopause is defined on the basis of potential vorticity), becomes vertical in the core of the jet stream, and then passes beneath the jet core. Reed and Danielsen (8) showed that the folded structure could be identified by its large values (stratospheric values) of potential vorticity and used the term "tropopause folding" to describe the process. Mass transports from the stratosphere were computed for several case studies of large-scale cyclogenesis in which the three-dimensional trajectories were determined from isentropic analysis. Danielsen (9) concluded, from these cases, that tropopause folding was an integral part of cyclogenesis. Therefore, the net seasonal and annual transport of mass from the stratosphere could be estimated by multiplying the mass transport per cyclogenesis by the number of cyclogenetic events. Danielsen calculated a mass transport value from the stratosphere to the troposphere of $(4.0 \pm 0.5) \times 10^{17}$ g during a 36-hour period over North America from January 2 to 3, 1958. A similar calculation for a cyclone of average intensity over North America from November 22 to 23, 1962, involved a total transfer of 6×10^{17} g from the stratosphere (10).

The amount of mass transported during these two events is in relatively good agreement. [Note: the total stratospheric mass in the northern hemisphere is of the order of $(4.5 \pm 0.5) \times 10^{20}$ g.] Danielsen's estimate of 4.3 $\times 10^{20}$ $g \cdot year^{-1}$ for the total northern hemispheric outflow due to large-scale eddy transport implies that a mass comparable to the entire northern hemispheric stratosphere is exchanged in 1 year. Reiter based his estimate for this annual outflow on a simple cyclone index proposed by Mahlman (11) (see Figure 7). During 1963 and 1964, the estimate of cyclonic activity yielded 22 and 23 respectively in the sector 70°-180°W. Reiter computed an annual transport of $6 \times 10^{17} \times 22.5 \times 3 = 4.5 \times 10^{19}$ g for the polar front jet-stream belt, at 40°-60°N in the northern hemisphere. Reiter assumes twice that amount, of exchange 800×10^{17} g, as a reasonable value for large-scale eddy transport from the stratosphere to the troposphere on an annual basis for the entire northern hemisphere. This is approximately 20% of the entire northern hemispheric stratosphere.

The numerical discrepancy (∿ 90% according to Danielsen versus ∿ 20% according to Reiter) is a consequence of inferring all this from a few events (well characterized and analyzed cyclogenetic case studies) and the global frequency, intensity, and duration of cyclogenesis. On the basis of strontium-90 concentrations measured in the lower stratosphere during 1959-1960 and 1962-1963, Danielsen (12) has deduced a mass outflow rate from the entire northern stratosphere:

$$\left(\frac{dM}{dt}\right)_{\text{outflow}} = a_1 + a_2 \cos \frac{2\pi}{\tau} (t - a_3) \qquad \text{(Eq. 1)}$$

where a_1: annual mean outflow rate [g yr^{-1}]

a_2: amplitude of annual mean [g yr^{-1}]

a_3: phase function

τ: 1 year

t: varies from 0 to 1 year

The numerical values are

$$\left(\frac{dM}{dt}\right)_{\text{outflow}} = [3.6 + 1.8 \cos 2\tau \, (t - \frac{4.5}{12})] \times 10^{20} \; (\text{g}\cdot\text{yr}^{-1}) \qquad \text{(Eq. 2)}$$

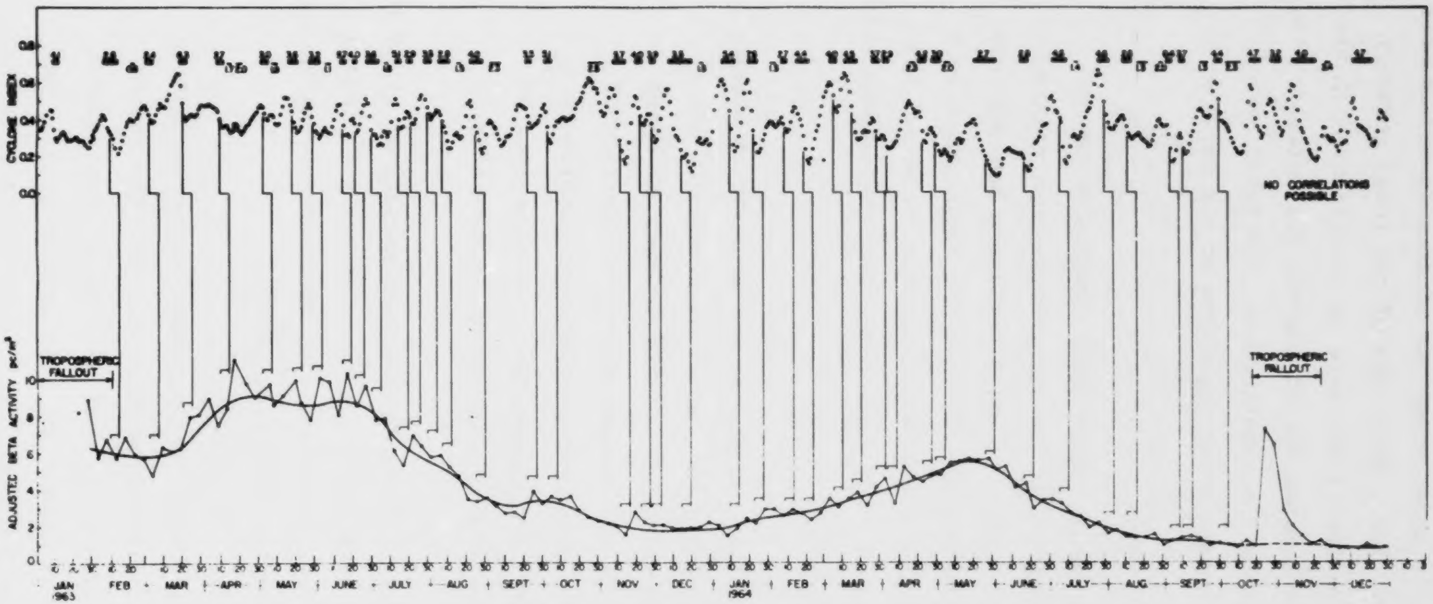


Figure 7. Time series of comparison between cyclone index and shorter period fallout fluctuations. Upper part of diagram is smoothed cyclone index series. In the lower part: thin connected lines are five-day mean age-adjusted gross beta activities: heavy smooth line gives mean monthly fallout values. Vertical lines from cyclone index show the high percentage of fallout increases within five days after rapid cyclone index decreases. Numbers across top of figure are values of $100\ (C_1 - C_2)/\Delta t$ computed during each cyclone index decrease. Numbers above heavy bars are greater than critical value of 2.5 and numbers below thin bars are below 2.5 (Mahlman, 1965b).

Source: "Large Scale Atmospheric Transport Processes of Radioactive Debris," by Elmar R. Reiter. Final Report Contract AT(11-1)-1340, Dept. of Atmospheric Science, Colorado State University, Fort Collins, CO, (COO-1340-8).

The maximum outflow in mid-April is three times the minimum in mid-October. The annual outflow is about $\frac{3.6}{4.5} = 0.80$, i.e., about 80% of the total northern hemisphere's stratospheric mass. (Danielsen's estimate is consistent with the total budget of atmospheric Sr^{90} as determined during project Springfield: the total amount of bomb debris injected into the stratosphere, the total amount present in the stratosphere, and the total amount deposited at the earth's surface are balanced by his analysis.)

On the basis of limited data available, there still remains large uncertainties on the total mass flow associated with large-scale eddy transport. As a consequence, it will be rather difficult to obtain reliable seasonal and annual estimates on the amount of ozone transported into the troposphere as a result of cyclonic activity. The foregoing analysis indicates, however, that this process plays a main role in transporting ozone from the stratosphere into the troposphere, as will be discussed later.

Relative to process *B*, Reiter (7) calculated the net decrease in stratospheric mass from winter to summer as 400×10^{17} g, which is roughly 10% of the mass of the northern hemispheric stratosphere. His estimate is based mainly on seasonal variation of average tropopause heights as function of latitude (see Figure 8). There are no estimates available in literature on the amount of ozone entrained into the troposphere due to the seasonal adjustments in tropopause levels. (Some new evidence is presented later.)

As an estimate of the magnitude of process *C*, the mean meridional circula--tion transport has been estimated by Reiter (7) to amount annually to 1633×10^{17} g, which is 38% of the mass of the stratosphere in the northern hemisphere. This meridional transport is mainly Hadley cell circulation.

The tropical segment of the Hadley cell is apparently very effective in introducing large amounts of tropospheric (ozone poor) air into the stratosphere. Continuity is retained as roughly the same amounts of stratospheric air will return into the troposphere in middle and high latitudes (7). Experimental evidence on the ozone intrusion into the troposphere attributable to the descending branches (for example the subtropical branch) of the mean meridional circulation is unavailable. Unlike the clear-cut tropopause folding events, which can be analyzed from routine radiosonde data, the mean meridional "circulation" is a parameterized concept of a very complex circulation system.

Examining process *D*, the mesoscale and small-scale eddy transport across the tropopause has been calculated by Reiter (7) to account for less than 1 to 5% of the total flux between stratosphere and troposphere (assuming a vertical eddy diffusivity value of $10^2\ cm^2 \cdot s^{-1}$). Ozone transport due to these sub-grid eddies is negligible, as will be discussed later.

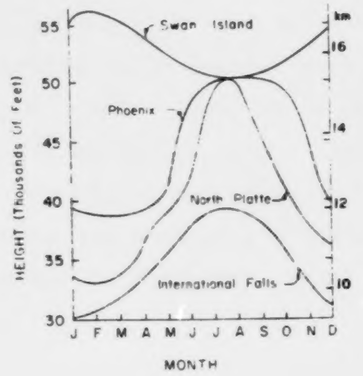


Figure 8. Average tropopause heights for the period 1946-1956 at Swan Island (17°N), Phoenix (33°N), North Platte (41°N), and International Falls (49°N) [Staley, 1962].

Source: "Stratospheric-Tropospheric Exchange Processes," E.R. Reiter. Reviews of Geophysics and Space Physics, 13, 4, Aug. 1975.

MEASUREMENTS FOCUSING ON STRATOSPHERIC-TROPOSPHERIC EXCHANGE PROCESSES

Measurements reported in the literature will be discussed as they relate to stratospheric ozone intrusions or as they relate to information on the stratospheric-tropospheric ozone flux.

Danielsen has presented overwhelming evidence that the mean potential vorticity, radioactivity, and ozone mixing ratios can be used as tracers for stratospheric air intrusions into the troposphere. Although each tracer has a different mid-stratospheric source, they develop a positive correlation in the lower stratosphere as a result of active adiabatic mixing (see Figures 9 and 10). Additional examples of fully analyzed tropopause folding events are shown in Figure 11 and Figure 12. The most recent study of three examples of tropopause folding (made in Project Duststorm during April 1975) (13) reinforced the conclusion (as did the flight data obtained during the operation of Project Springfield), that ozone-rich air is transported into the troposphere with each major cyclonic development. Ozone mixing ratios have been measured in Project Duststorm down to 20,000 feet, but no attempts have been made to follow the intruded stratospheric air as it mixes downward and (eventually) impacts on the ground. Such direct experimental evidence has not been reported in the literature.

Assuming a stratospheric mass outflow of (4 to 6) x 10^{17} g per cyclonic event and an ozone mass mixing ratio of 1.3 x 10^{6} g/g in the lower stratosphere would yield an amount of (5.2 to 7.8) x 10^{11} g ozone transported into the troposphere during each cyclonic event. If one follows Reiter's argument in arriving at the northern hemispheric mass flux due to large-scale eddy transport as outlined under *A* above, the annual outflow of ozone would amount to: 1.3 x 10^{6} $(g \cdot g^{-1})$ x 6 x 10^{17} (g) x 22.5 (cyclonic events for 40°-60°N, 70°-180°W) x 3 (for full circumference) x 2 (for all latitudes) = 1.05 x 10^{14} g of ozone resulting from process *A*, and 1.3 x 10^{6} $(g \cdot g^{-1})$ x 1633 x 10^{17} g = 2.12 x 10^{14} g of ozone resulting from transport process *B* outlined above.

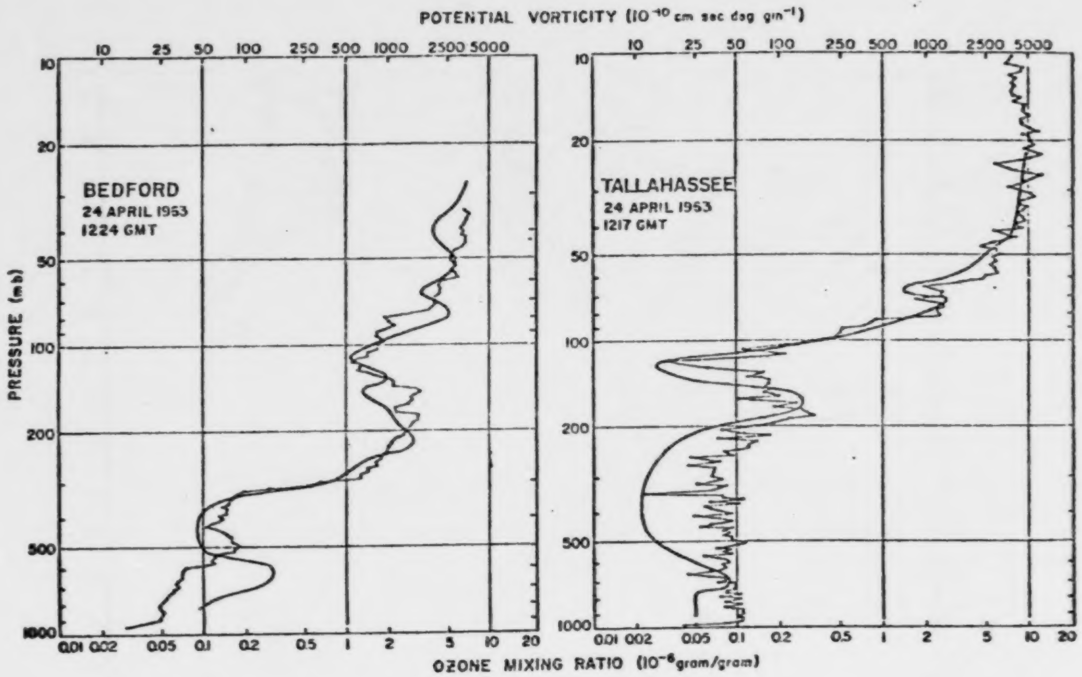


Figure 9. Vertical profiles of ozone mixing ratio (thin line) and potential vorticity (heavy line) derived from Figure 12 for Bedford, Mass., and Tallahassee, Fla., 1200 GMT 24 April 1963.

Source: "Stratospheric-Tropospheric Exchange Based on Radioactivity, Ozone and Potential Vorticity," by Edwin F. Danielsen. J. of the Atmospheric Sciences, Vol. 25, pp. 502-518.

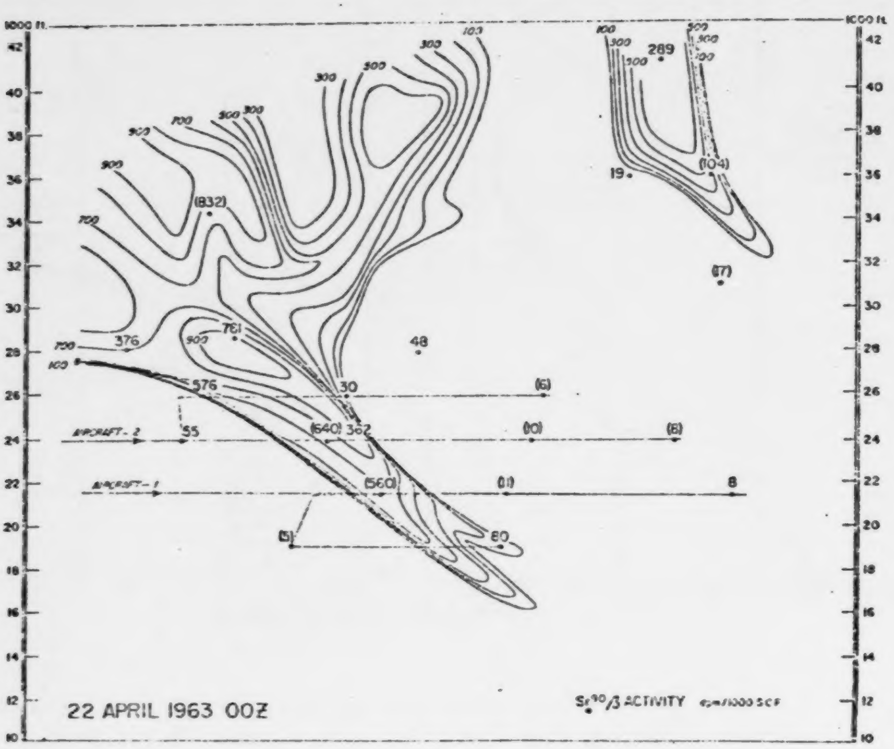


Figure 10. Potential vorticity (contoured at intervals of 100 x 10^{-10} cm sec (°K gm^{-1}) computed from Figure 2 and β activity of Sr^{90} (dpm/KSCF).

Source: "Stratospheric-Tropospheric Exchange Based on Radioactivity, Ozone and Potential Vorticity," E. Danielsen. J. of the Atmospheric Sciences, 25.

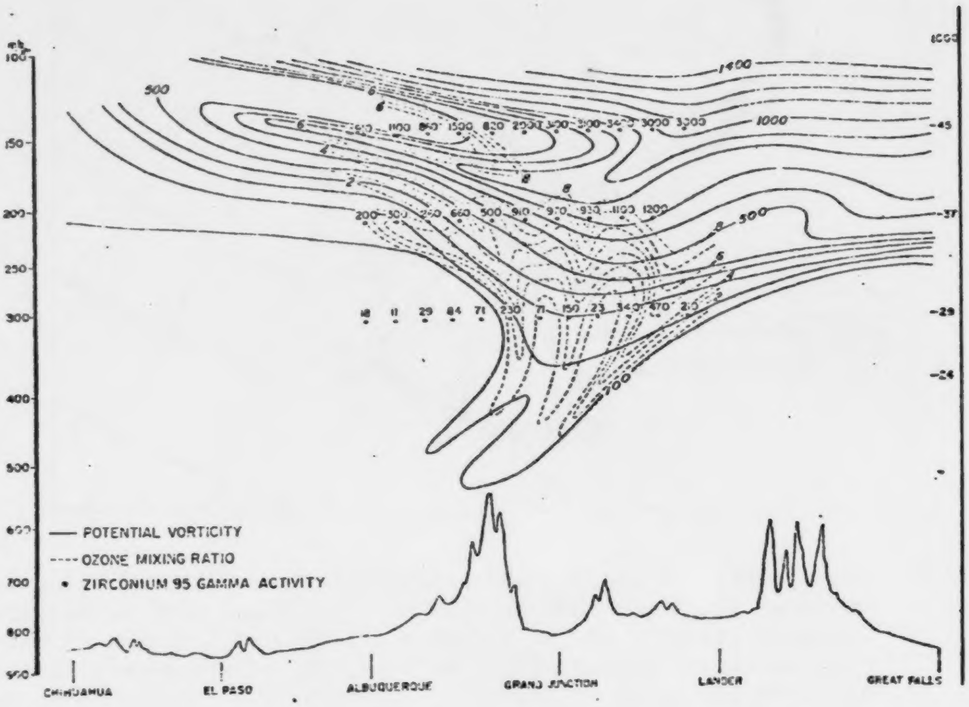
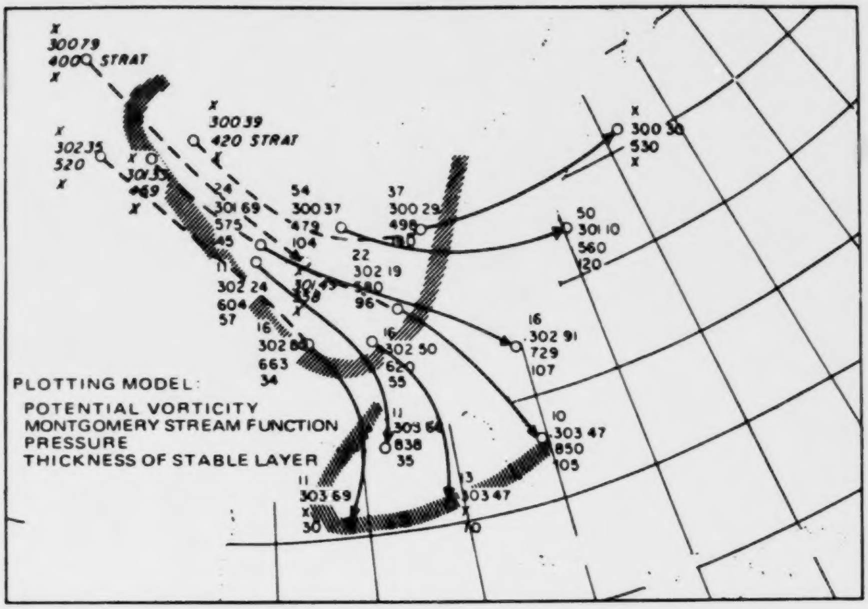


Figure 11. Vertical cross-section of potential vorticity in units of 10^{-10} cm sec deg g^{-1}. Zirconium 95 activities in units of dpm $(SCF)^{-1}$ are plotted above the sampling points, with additional isoline of ozone mixing ratio in units of 10^{-7} g g^{-1} (dashed lines).

Source: "Observed Distribution of Radioactivity, Ozone, and Potential Vorticity Associated with Tropopause Folding," E. Danielsen, et al. J. of Geophysical Research, 75, 12, April 20, 1970.


30079
400 STRAT
30039
420 STRAT
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469
24
30169
575
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104
37
30029
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50
30110
560
120
300
530
22
30219
96
11
30224
604
57
16
663
34
16
30250
55
16
30291
729
107
PLOTTING MODEL:
POTENTIAL VORTICITY
MONTGOMERY STREAM FUNCTION
PRESSURE
THICKNESS OF STABLE LAYER
11
838
35
10
30347
850
105
11
30369
30
13
30347

Figure 12. Trajectories on the 300°K isentropic surface. Dashed lines are November 22, 1962, 0000 to 1200 UT; full lines with arrows are November 22, 1200 UT, to November 23, 0000 UT. Values of potential vorticity (units of 10^9 cm s deg/g), of Montgomery stream function (units of 10^7 cm^2/s^2), of pressure of the 300°K surface (millibars), and of thickness of the stable layer (millibars) are entered according to the plotting model; slanting numbers are for November 22, 0000 UT, and vertical numbers are for other map times. The centers of the hatched band mark boundaries on November 22, 1200 UT, and November 23, 0000 UT, of stratospheric air from the tropopause level that reaches the ground over the southern United States [Reiter and Mahlman, 1964].

Source: "Stratospheric-Tropospheric Exchange Processes," E.R. Reiter. Reviews of Geophysics and Space Physics, 13, 4, Aug. 1975.

Hering and Borden (14) have derived an expression for the ozone mass mixing ratio in the lower stratosphere:

$$\chi_m = [1.3 = 0.3 \cos \frac{2\pi}{\tau} (t - \frac{4.5}{12})] \times 10^6 g \cdot g^{-1} \qquad \text{(Eq. 3)}$$

The product of Danielsen's mass outflow rate expressed in Equation 2 and Equation 3 predicts an annual outflow of 4.7 x 10^{14} g of ozone for the northern hemisphere.

Summation of all these arguments produces these estimates for the annual outflow of ozone from the stratosphere over the northern hemisphere:

- Danielsen (large scale cyclogenesis): 4.7 x 10^{14} g of ozone
- Reiter (large scale cyclogenesis and Hartley circulation):
  3.2 x 10^{14} g of ozone

Note that neither of these values of vertical ozone transport across the tropopause boundary were measured directly. Note also that the assumed ozone mass mixing ratio of 1.3 x 10^{-6} $g \cdot g^{-1}$ for the lower stratosphere enters critically in these annual flux calculations. Taking all uncertainties into account, the true annual flux is probably in the range of 2 to 8 x 10^{14} g of ozone, a significant portion of this being introduced in the latitude belt 30° to 60°N.

Ozone measurements taken from commercial airliners (NASA Global Atmospheric Sampling Program, GASP) offer an opportunity for establishing an ozone climatology along major flight corridors. Table 1 shows pertinent data statistics for the sampling period March 1975 through March 1976. Nastrom (15) has presented a comprehensive analysis of these GASP data (archived on tapes VL0001-VL0004). The bulk of the flights were within the continental United States, from the mainland to Hawaii, and from the United States to Europe. The *in situ* ozone mixing ratio, measured by an ultraviolet absorption photometer, is reported every 5 minutes (i.e., about every 75 km, but every other observation is missed because the instrument is in a calibration mode).

Most observations were taken between 10-12 km altitude. Flight level atmospheric pressure, temperature, wind direction and speed, and an indication from the aircraft accelerometer of turbulence occurrence, are reported with each ozone observation. Supplementary parameters were computed for each ozone observation from the NMC northern hemisphere grids of isobaric height fields and tropopause pressure fields. Tropopause separation pressure ($P_{tropopause} - P_{aircraft}$), geostrophic winds and vorticity, potential vorticity, and the algebraic sign of the vertical velocity were also computed.

TABLE 1. SUMMARY OF GASP DATA

Month	Total Flights	Total Obs.	Latitude Range	Longitude Range
Mar 1975	57	1263	9N-61N	180E-180W
Apr	26	554	19N-47N	75W-159W
May	66	1625	23S-47N	45W-114E
Jun	35	908	19N-45N	84W-159W
Jul	3	78	21N-41N	84W-159W
Aug	16	434	21N-47N	84W-159W
Sep	23	579	21N-43N	75W-159W
Oct	25	716	21N-43N	75W-159W
Dec	10	326	21N-45N	72W-156W
Jan 1976	36	1119	9N-61N	180E-180W
Feb	54	1435	33S-43N	72W-114E
Mar	39	1057	9N-57N	180E-180W

Source: "Variability and Transport of Ozone at the Tropopause from the First Year of GASP Data," by G. D. Nastrom, Control Data Corp., Research Report No.4, Feb. 22, 1977, Contract NAS 2-7807 for NASA-Lewis Research Center.

Nastrom compared mean ozone values from GASP flights with those from North American ozonesondes and found them compatible, establishing confidence for the NASA GASP data (see Figure 13). Monthly mean values of ozone and potential vorticity are compared in Figure 14. As Danielsen, Hering, and others have found, there exists a close correspondence of the two fields (correlation coefficient = 0.95). Particularly notable are the apparent intrusions of ozone and potential vorticity below the tropopause near 40°N. Nastrom has also calculated the vertical flux of ozone: all ozone observations taken within 50 hPa of the tropopause and north of 30°N were sorted according to the sign of the associated vertical motion. To estimate the magnitude of the flux, the mean magnitude of the vertical velocity at the tropopause has to be assumed, for which a value of $|\overline{w}| = 0.5\ \mathrm{cm \cdot s^{-1}}$ is adapted. With the assumed $|\overline{w}|$ value, the average annual flux across the tropopause amounts to $6.2 \times 10^{-12}\ (\mathrm{g \cdot cm^{-2} \cdot s^{-1}})$

$$\{([O_3]\uparrow - [O_3]\downarrow)(\mathrm{ppbv}) \times 1.656 \left(\frac{\mathrm{g\ ozone}}{\mathrm{g\ air}}\right) \times \delta_{\mathrm{density}} \left(\frac{\mathrm{g\ air}}{\mathrm{cm^3}}\right) \times |\overline{w}| \left(\frac{\mathrm{cm}}{\mathrm{sec}}\right)\}$$

or 7.8×10^{10} molecules $\mathrm{cm^{-2} \cdot s^{-1}}$. This vertical ozone transport estimate reflects only the transport by motions whose wavelength is longer than about 700 km (large-scale eddy transport, Process A).

The annual flux of 7.8×10^{10} molecules$\cdot\mathrm{cm^{-2} s^{-1}}$ compares very well with the results of Fabian and Pruchniewicz (16) derived on the basis of surface ozone measurements (see Table 2).

The transport of ozone by disturbances smaller than about 700 km (small-scale eddy transport, Process C) was estimated by Nastrom by assuming the flux is the product of an eddy diffusion coefficient and the gradient of ozone across the tropopause. The diffusion coefficient at the tropopause used by Cunnold et al. (17) — $K_z = 3 \times 10^3\ \mathrm{cm^2 s^{-1}}$ — was adopted, and the gradient of ozone was estimated by finite differences of mean values of layers 50 hPa thick and centered 25 hPa above and below the tropopause. The resulting estimates of the diffusive flux (Process C) are only about 3% as large as the corresponding fluxes by large-scale motions (Process A) (see Table 2). Similar

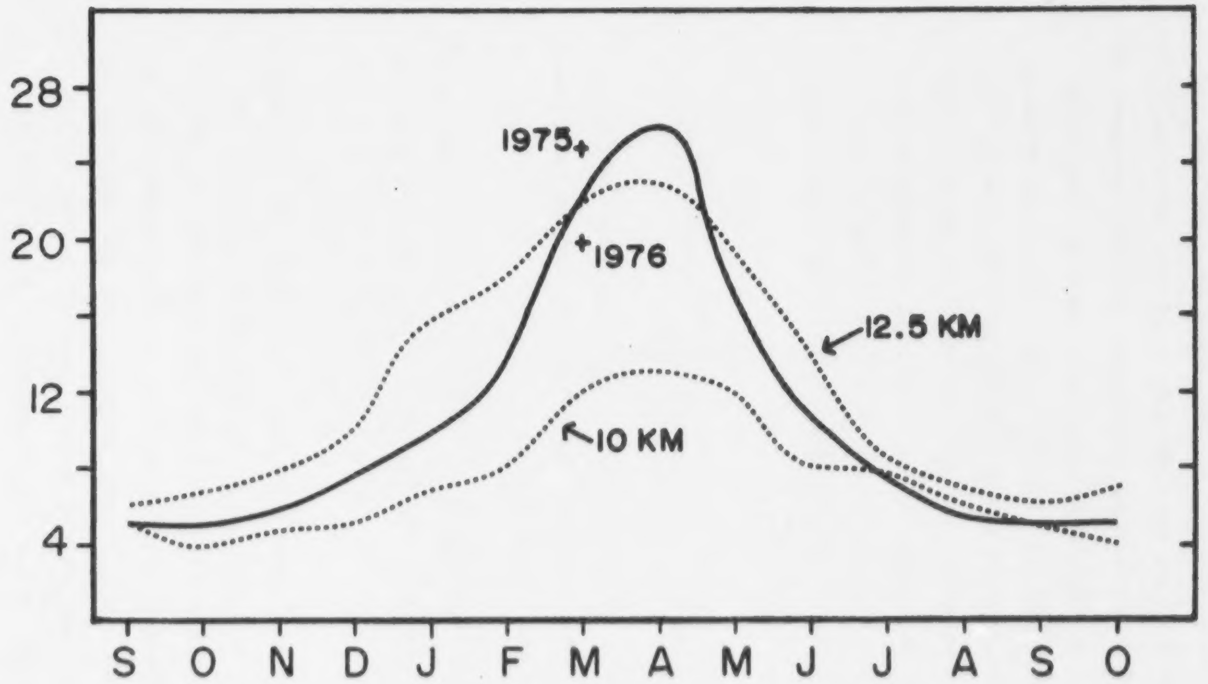

Figure 13. Heavy line is monthly mean variation of GASP ozone at 11-12 km, 36-42°N from March, 1975, through March, 1976. A 1-2-1 smoothing has been applied. Dotted lines are ozonesonde means at 40°N from Wilcox, et al. (1975). Units: 10^{11} molecules cm^{-3}.

Source: G.D. Nastrom: "Variability and Transport of Ozone at the Tropopause from the First Year of GASP Data." Control Data Corp., Research Report No. 4, Feb. 22, 1977, Contract NAS 2-7807 for NASA-Lewis Research Center.

R. Wilcox, G. Nastrom and A. Belmont: "Periodic Analysis of Total Ozone and its Vertical Distribution." NASA-CR-137737, 51 pp. Available from NTIS, Abstract No. N75-32657.

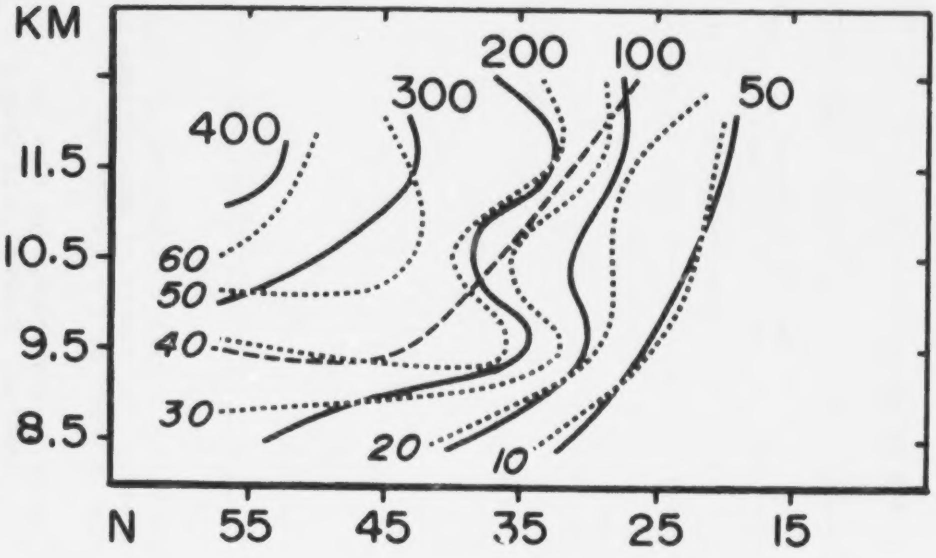

Figure 14. Solid lines are "zonal" means of ozone (ppbv) at 10° latitude belts for combined March data (1975 and 1976). The dashed line is mean tropopause location, and the dotted lines are "zonal" means of potential vorticity (10^{-6} deg hPa^{-1} s^{-1}), for each belt.

Source: "Variability and Transport of Ozone at the Tropopause from the First Year of GASP Data," G.D. Nastrom. Control Data Corp., Research Report No. 4, Feb. 22, 1977, Contract NAS 2-7807 for NASA-Lewis Research Center.

TABLE 2. OZONE MIXING RATIO

	Mean Ozone (ppbv) Upward Motion	Mean Ozone (ppbv) Downward Motion	Mean Air Density (10^{-4} g cm^{-3})	Net Flux (based on $\lvert\overline{w}\rvert$ = 0.5 cm s^{-1} (10^{10} molec $cm^{-2}s^{-1}$)	Diffusive Flux (10^{10} molec $cm^{-2}s^{-1}$)
Winter	68.0	79.6	3.75	9.0	0.24
DJF	(887)	(907)			
Spring	214.7	227.3	3.63	9.5	0.25
MAM	(769)	(758)			
Summer	143.5	155.0	3.30	7.9	0.13
JJA	(126)	(126)			
Autumn	73.5	80.6	3.19	4.7	0.11
SON	(231)	(151)			
			Average	7.8	0.18

Ozone mixing ratio, Trop-50 hPa to Trop+50 hPa, sorted according to the sign of w. Only data north of 30°N are used here. The number of observations is given in parentheses. The diffusive flux is based on K = 3 x 10^3 cm^2 s^{-1}.

Source: "Variability and Transport of Ozone at the Tropopause from the First Year of GASP Data," by G.D. Nastrom. Control Data Corp., Research Report No. 4, Feb. 22, 1977, Contract NAS 2-7807 for NASA-Lewis Research Center.

results for the total mass transport across the tropopause have been obtained by Reiter, as pointed out earlier (although Reiter used a K_z value of 10^2 cm^2 s^{-1}).

Nastrom's results are the first direct estimates of the ozone flux across the tropopause (the main assumption being the representative $|\overline{w}|$ value). The detailed mechanism whereby this flux occurs, such as done by Danielsen and Reiter, cannot be derived directly from the GASP data because the NMC grid is too coarse to resolve folds in the tropopause. This detailed transfer mechanism is not critical if the downward transport of ozone is associated with large-scale motions and can be parameterized by a representative $|\overline{w}|$ value.

If one assumes that the ozone flux of 7.8×10^{10} molecules$\cdot cm^2 \cdot s^{-1}$ (deduced from direct ozone observations at 10-12 km altitude, 30°-60°N and mainly over the U.S.) is a representative average for the northern hemisphere, it would yield an annual ozone mass flow into the troposphere of 4.9×10^{14} g.

There exists some discrepancy in literature with respect to the relative importance of ozone transport into the troposphere via large-scale eddies (Process A, mainly cyclonic activity) versus mean meridional circulation (Process D), which cannot be resolved at this time on the basis of available experimental data. Some information is available, however, from the U.C.L.A. General Circulation Model of Mintz and Schlesinger (18). This is a three-dimensional, global atmospheric general-circulation model that extends from the earth's surface to the stratopause. Its circulation, radiational heating, and ozone photochemistry are fully coupled and interactive. Their results of computations to date are:

- In the zonal average, the largest vertical transport of ozone is in the descending branches of the mean meridional circulation, but in the global average, the vertical eddy transport of ozone is several times larger than the vertical transport by the mean meridional circulation (see Figure 15).

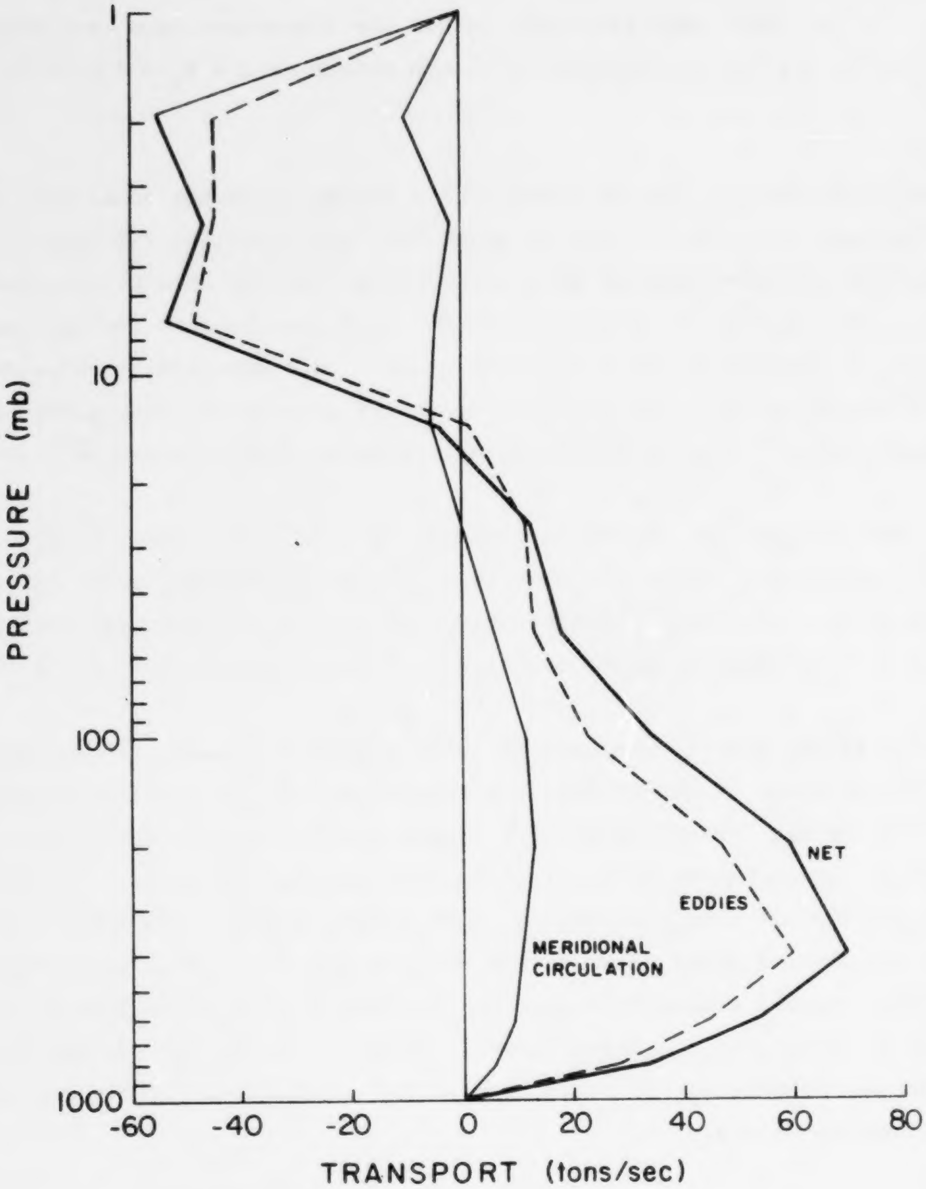

Figure 15. Vertical profiles of the global vertical ozone transport. Positive values are downward.

Source: "Ozone production and transport with the U.C.L.A. general circulation model," Y. Mintz and M. Schlesinger. Proceedings of the 4th Conference on the Climatic Impact Assessment Program. Edited by T. Hard and A.J. Broderick. DOT-TST-75-38, 201-222, February (1975).

- The vertically-integrated, latitudinal transport of ozone in the tropics consists almost entirely of a large-scale transport from the summer to the winter hemisphere by the mean meridional circulation, but in the middle and higher latitudes it is the small difference between a large poleward transport by the eddies and a large equatorward transport by the mean meridional circulation.

- The vertically integrated latitudinal transport by the eddies is, itself, the small difference between a large eddy transport toward the poles in the middle and lower stratosphere and a large eddy transport toward the equator in the upper and middle stratosphere.

[Note: Mintz and Schlesinger's model also shows the baroclinic waves for the 500 mb geopotential height field which move slowly eastward. By superimposing the trough and ridge lines of these waves on the total ozone field, the model shows that the maxima and minima of total ozone coincide, respectively, with the trough and ridge lines of the 500 mb waves. Both the amplitude of this zonal variation of total ozone and its phase relationship to the baroclinic disturbances at 500 mb (and at 300 mb) are precisely what is observed in the real atmosphere, as shown for example by Normand (19).]

MEASUREMENTS OF THE REPRESENTATIVE GROUND-LEVEL OZONE CONCENTRATIONS

Junge (20) presented a comprehensive assessment and analysis of existing ozone data and arrived at a global ozone budget based on ground-level ozone observations, on ozone surface destruction rates, and on estimations of stratospheric-tropospheric exchange processes.

Junge's analysis is based on the assumption that tropospheric ozone in the northern hemisphere and its seasonal variation can be approximated by an expression of the form:

$$\theta = a_1 + a_2 \sin[\omega(t - a_3)] \text{ (tons)} \qquad \text{(Eq. 4)}$$

where a_1: annual mean for θ, the total tropospheric ozone content

a_2: amplitude

a_3: phase function

ω: $2\pi/\tau$ and $\tau = 1$ year

t: 0-1 year

To determine the parameters a_1 and a_2 in Equation 4, it is imperative to obtain representative values for the tropospheric ozone and its seasonal variation.

Junge points out that data obtained at or near the earth's surface are usually affected by ozone destruction at or near the ground. Average concentrations of ozone near the ground are thus of little value for general considerations because they more or less reflect the microclimatological conditions of the sampling site. The daily maximum values of ozone usually occur around noon when vertical mixing is strongest and when the influence of the surface destruction layer is minimized. It can be expected that these values are approximately representative for ozone in the undisturbed troposphere in areas which are free of air pollution. In polluted air, ozone destruction is of considerable magnitude within the air. In reducing atmospheres, such as in the planetary boundary layer over central Europe, the maximum ozone values are usually lower than in the layers aloft. Junge's careful search for proper ozone measuring sites to obtain tropospheric background ozone concentration was reinforced later by Dutsch (4):

> As the ground is thought to be the main sink for stratosphere-borne ozone, it is hoped that the measurements of ozone at the surface could give additional useful information on the atmospheric ozone budget. This is, however, only the case if it is possible to obtain from such continuous registration inference on the ozone concentration of the lower troposphere above the planetary boundary layer. Very careful selection of sites free from any pollution and from influences of inversions is needed. Mountain stations would seem especially useful but even there, disturbances by local circulation effects are indicated. Careful comparison with available sounding series may lead to useful concepts for finally evaluating destruction near the surface in connection with surface structure on one side and with stratospheric-tropospheric ozone transfer on the other side.

Junge selected for his analysis three mountain stations:

Arosa (47°N, 1860 MSL)
Mauna Loa (20°N, 3000 MSL)
Srinagar, North India (34°N, 1700 MSL)

He calculated monthly average values of daily maximum ozone concentration (see Figure 16). The annual mean concentration for these stations is taken as 50 $\mu g \cdot m^{-3}$, which fixes the annual average for the total tropopause ozone content $a_1 = 1.30 \times 10^8$ tons ozone. (Based on an average tropopause height of 12 km, and an ozone mixing ratio increasing linearly by a factor of two as height increases from 1 km to 12 km.) The amplitude of the yearly variation of ozone for the representative stations (Figure 16) is about ± 15 $\mu g \cdot m^{-3}$ which results in $a_2 = 0.39 \times 10^8$ tons ozone. Junge observes from total ozone column measurements (most of the mass of which is in the stratosphere) at Arosa and Mauna Loa and from the calculated total northern hemispheric total ozone (see Figure 16) that the phase of the surface ozone is somewhat delayed against that of total (mainly stratospheric) ozone. He interprets this time delay as the result of a limited lifetime of tropospheric ozone. Junge formulates a budget equation with the following assumptions: ozone destruction occurs primarily at or near the ground; the rate of ozone destruction, D, is approximately proportional to the ozone concentration and thus proportional to the total tropospheric ozone content, θ, as presented in Equation 4.

$$D = -C_o \theta \ (\text{tons} \cdot \text{yr}^{-1}) \qquad \text{(Eq. 5)}$$

$$(\text{tropospheric lifetime } \tau = C_o^{-1})$$

From Equations 4 and 5 it follows that the rate of injection, I, of stratospheric ozone into the troposphere must have the form

$$I = C_1 + C_2 \sin(\omega t) \ (\text{tons} \cdot \text{yr}^{-1}) \qquad \text{(Eq. 6)}$$

where t = 0 is not identical to the beginning of the calendar year. The phase difference between I and θ is taken into account by a_3 in Equation 4. Combining Equations 5 and 6 results in the budget equation

$$\frac{d\theta}{dt} = I + D = C_1 + C_2 \sin(\omega t) - C_o\theta \qquad \text{(Eq. 7)}$$

with the solution

$$\theta = \frac{C_1}{C_o} + \frac{C_2}{\omega}\left[\left(\frac{C_o}{\omega}\right)^2 + 1\right]^{-\frac{1}{2}} \sin\left[\omega t - \text{arc sin}\left(\frac{C_o}{\omega^2} + 1\right)^{-\frac{1}{2}}\right] \qquad \text{(Eq. 8)}$$

Direct comparison of Equations 8 and 4 yields

$$a_1 = \frac{C_1}{C_o} \qquad \text{(Eq. 9)}$$

$$a_2 = \frac{C_2}{\omega}\left(\frac{C_o}{\omega^2} + 1\right)^{-\frac{1}{2}} \qquad \text{(Eq. 10)}$$

$$a_3 = \frac{1}{\omega}\,\text{arc sin}\left(\frac{C_o}{\omega^2} + 1\right)^{-\frac{1}{2}} \qquad \text{(Eq. 11)}$$

from which C_o, C_1 and C_2 can be calculated.

Junge recognized that the delay time a_3 (phase) is the most uncertain value. It can be taken from observations if one assumes that the injection rate I is in phase with the total ozone burden of the stratosphere, which is only a very rough approximation. By evaluating the gross fission product concentration in surface air averaged for the northern hemisphere according to Equations 8 through 11 and taking for C_o the experimentally established value of 12 yr^{-1} (the tropospheric lifetime of radioactive aerosol is of the order of 1 month) yields a time delay of a_3 = 0.9 month between I (fission products) and θ (fission products).

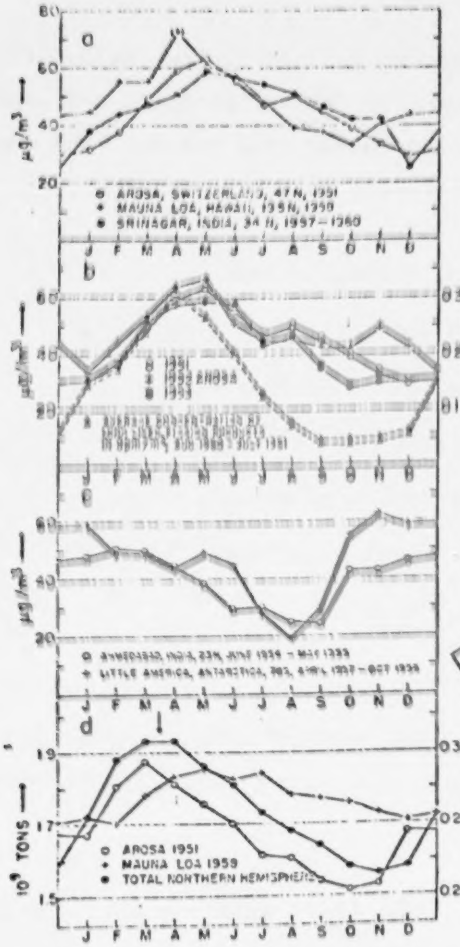

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Figure 16. Annual variation of monthly average values of daily maximum ozone concentration at various places. (a) Values for Arosa 1800 m above sea level (Gotz & Volz, 1951), Mauna Loa 3000 m above sea level (Price & Pales, 1959, 1961) and Srinagar 1700 m above sea level (Ramanathan, 1961). The value in April at Mauna Loa is based on a few days only. (b) Values for three consecutive years in Arosa, 1951 (Gotz & Volz, 1951) and 1952 and 1953 (Volz & Perl, 1961). For comparison the average monthly concentration of long lived fission products in surface air for the northern hemisphere obtained from the 80th Meridian Network data (Lockhart, 1961). (c) Values for Ahmedabad 50 m above sea level (Dave, 1961) and Little America 50 m above sea level (Wexler et al., 1960). (d) Total ozone for Arosa (Gotz & Volz, 1951) Mauna Loa (Price & Pales, 1959, 1961) and the integrated average value based on data by Dutsch (1946) after correction for newer absorbtion data (Dutsch, 1959).

Source: Junge, C.E.: "Global ozone budget and exchange between stratosphere and troposphere," Tellus V XIV, 4 (1962).

Since there appeared to be another time delay of 1 month between the spring maximum of radioactive fallout products and ozone (see Figure 16), Junge took the a_3 value for ozone as 2 months. The numerical values for the ozone budget are therefore (northern hemisphere):

Stratospheric ozone injection rate

$$I = [4.7 - 2.8 \sin (\omega t)] \times 10^{14} \ (g \cdot yr^{-1})$$

ozone flux = 7.5×10^{10} molecules$\cdot$cm^{-2} s^{-1}

annual ozone mass flow into troposphere

$$= 4.7 \times 10^{14} \text{ g of ozone}$$

average tropospheric residence time for ozone

$$\tau_t = c_o^{-1} = 3.3 \text{ months}$$

Junge was first to present a thorough analysis of the ozone budget based on a carefully selected and representative tropospheric ozone data base. Earlier estimates, also based on tropospheric ozone observations, are compatible with Junge's results:

Kroening and Ney (21): ozone flux = 6×10^{10} molecules cm^{-2} s^{-1}

Paetzold (22): ozone flux = $(2.5 - 5) \times 10^{10}$ molecules cm^{-2} s^{-1}

Junge (20) proposed the establishment of a meridional network of representative surface ozone recording stations, which should be maintained for several years. This would provide better data for a_3 (phase) and may also show small systematic differences of the delay time, which can provide information on the injection rate as a function of latitude and, perhaps, longitude.

This network was established in 1969 under Project "Tropospharisches Ozon" by Fabian and Pruchniewicz (16). Permanent registration of ozone at ground level was obtained from 16 stations, located on a meridional chain between 69.5°N and 34°S, centered between 10 and 20 degrees longitude east (see Table 3). The instruments were installed at sites with relatively clean

TABLE 3. LIST OF STATIONS OF PROJECT TROZ

Station	Latitude	Institution maintaining station	Time of operation
Tromsö	69.5°N	Auroral Observatory Tromsö	Aug. 1970 - present
Bredkälen	63°N	University of Stockholm	Dec. 1968 - Jan. 1970
Kise	60°N	Staten Experiment Station	Aug. 1970 - Nov. 1972
Westerland	55°N	Bioklimat. Forschungestelle Univ. Kiel	July 1971 - present
Norderney	53.5°N	Wetterwarte, Deutscher Wetterdienst	July 1969 - present
Lindau	52°N	MPI für Aeronomie	Jan. 1969 - present
Hohenpeissenberg	48°N	Met. Observatorium, Deutscher Wetterdienst	Jan. 1969 - May 1972
Zugspitze	47.5°N	Inst.f.Umweltforsch. Garmisch	Jan. 1969 - present
Cagliari	38°N	Aeronautica Militare, OSSMA	Sept. 1970 - present
Kairouan	36°N	Service Météo. de la Tunisie	Nov. 1970 - present
Fort-Lamy (Ndjamena)	12°N	ASECNA	Sept. 1970 - June 1974
Luanda	9°S	Servico Meteorologico de Angola	Oct. 1970 - present (no contact since mid-1975)
Sa da Bandeira	15°S	Servico Meteorologico de Angola	Oct. 1970 - present (no contact since mid-1975)
Windhoek	23°S	Weather Bureau, Met. Station	Nov. 1970 - present
Alexander Bay	28°S	Weather Bureau, Met. Station	Nov. 1970 - May 1974
Hermanus	34°S	Magnetic Observatory CSIR	Sept. 1970 - present

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P.G. Pruchniewicz. Contract no. FA-62/1 Deutsche Forschungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

air conditions. Several general conclusions can be drawn from the long-term ozone observations (16) which confirm Junge's earlier observations and which are very relevant to recent discussions focusing on "photochemical production of ozone versus ozone transport."

a. The diurnal variations of ozone concentrations exhibit regular features characteristic of the particular stations. Low ozone values near the ground indicate weak or stagnant vertical exchange of the surface layer with the free adiabatic troposphere, while the daily maxima appear when ozone-rich air from the free troposphere reaches the ground station. Typical continental stations with convective mixing during the day (Fort Lamy, Sa da Bandeira) show the daily maximum around noon, when this convection is strongest (see Figure 17). At mountain stations (Zugspitze) the maximum occurs during the night due to the small-scale mountain circulation pattern (Katabatic wind flow). Coastline stations governed by land-sea circulation (Westerland, Norderney, Alexander Bay) show the daily maximum during evening and night.

b. The ozone daily maximum values from ground stations are representative of the ozone concentration of the free troposphere. This was shown by studying the "Austausch-coefficient" of the near surface layer using a 120 m tower (Tsumeb, S.W. Africa). The area surrounding the tower is covered with a homogeneous covering of brushy vegetation for thousands of square kilometers. Correlation coefficients of 0.40 between $[O_3]$ at 5 m and $[O_3]$ at 100 m above surface were obtained under stable conditions (Ri [Richardson number]> 0) versus 0.95 for unstable (Ri < 0) conditions (see Figure 18).

Several investigators (23-26) have interpreted part of all of the ozone variation they observed on the basis of the phenomena described in (a) and (b) above. The comprehensive and quantitative analysis of Fabian and Pruchniewicz of the impact of surfaces and of "reducing atmospheres" on the ozone concentration within the planetary boundary layer (acting as an ozone sink) implies that photochemical production is not the only mechanism to explain the com-

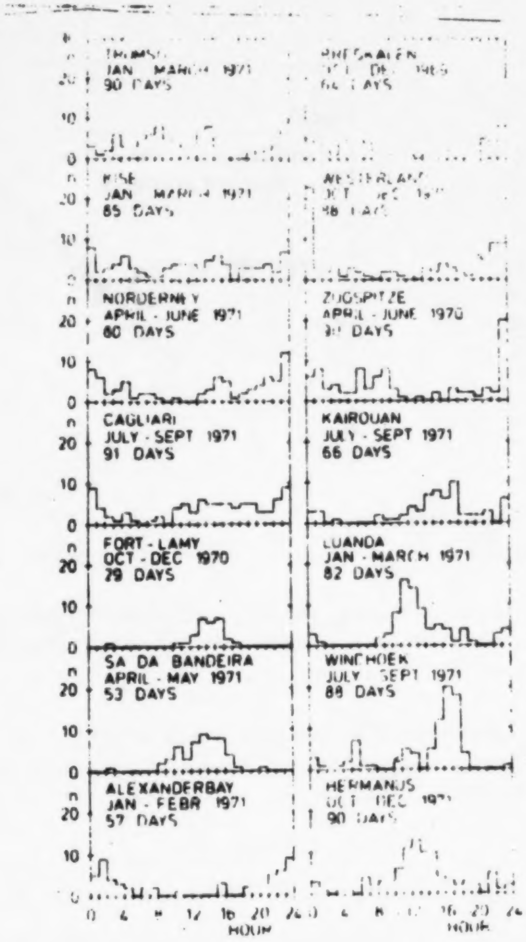

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Figure 17: Probability of the occurrence of the daily maximum of ozone near the ground over hourly intervals. n denotes the number of days out of the total given in the headlines when the daily maximum occurs at given hourly intervals.

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P.G. Pruchniewicz. Contract No. FA-62/1 Deutsche Forschungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

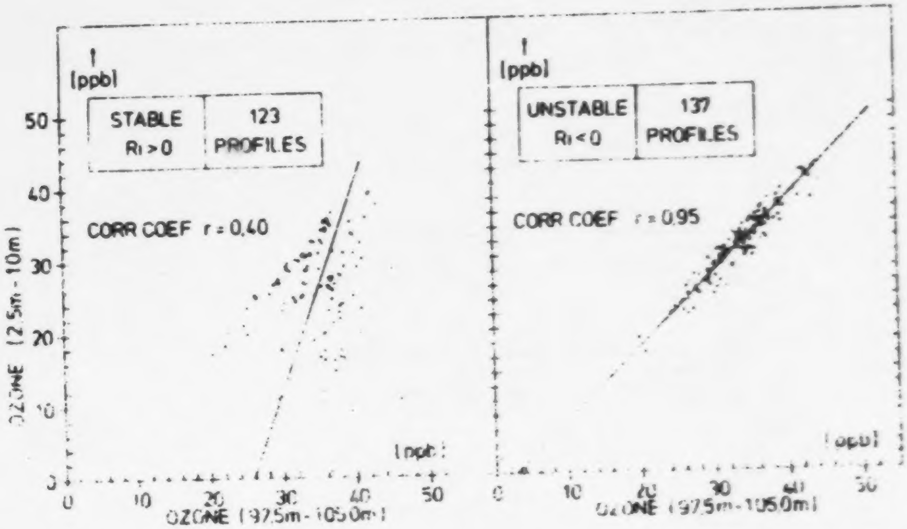


Figure 18. Correlation of mean ozone values measured within the Prandtl layer (2.5-10m) with ozone concentration of the layer between 97.5 and 105 m.

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P.G. Pruchniewicz. Contract No. FA 62/1 Deutsche Forschungsgame-inschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

monly observed diurnal variation in ozone concentration. The monthly means of tropospheric ozone, computed from the surface ozone daily maxima for Fabian and Pruchniewicz's meridional network are shown in Figure 19. The annual variations are fairly regular, and nearly all stations exhibit a pronounced annual sinusoidal wave pattern with characteristic mean, amplitude, and phase throughout the time of observation (see Table 4, a harmonic analysis of the annual variation was performed). The average meridional distribution of ozone in the troposphere varies by a factor of about 2 between the lowest values in the tropics and the highest values observed in the subtropical regions and northern mid-latitudes. This decreasing trend in ozone concentration towards the equator is especially pronounced at high altitudes (11 km) as Holdeman and Humenik (27) showed from the analysis of NASA-GASP data (see Figure 20). The phase a_3 of the annual maximum shows a clear variation with latitude (see Table 4). The annual maximum which occurs during April/May in high northern latitudes is shifted towards July in northern mid-latitudes and it appears

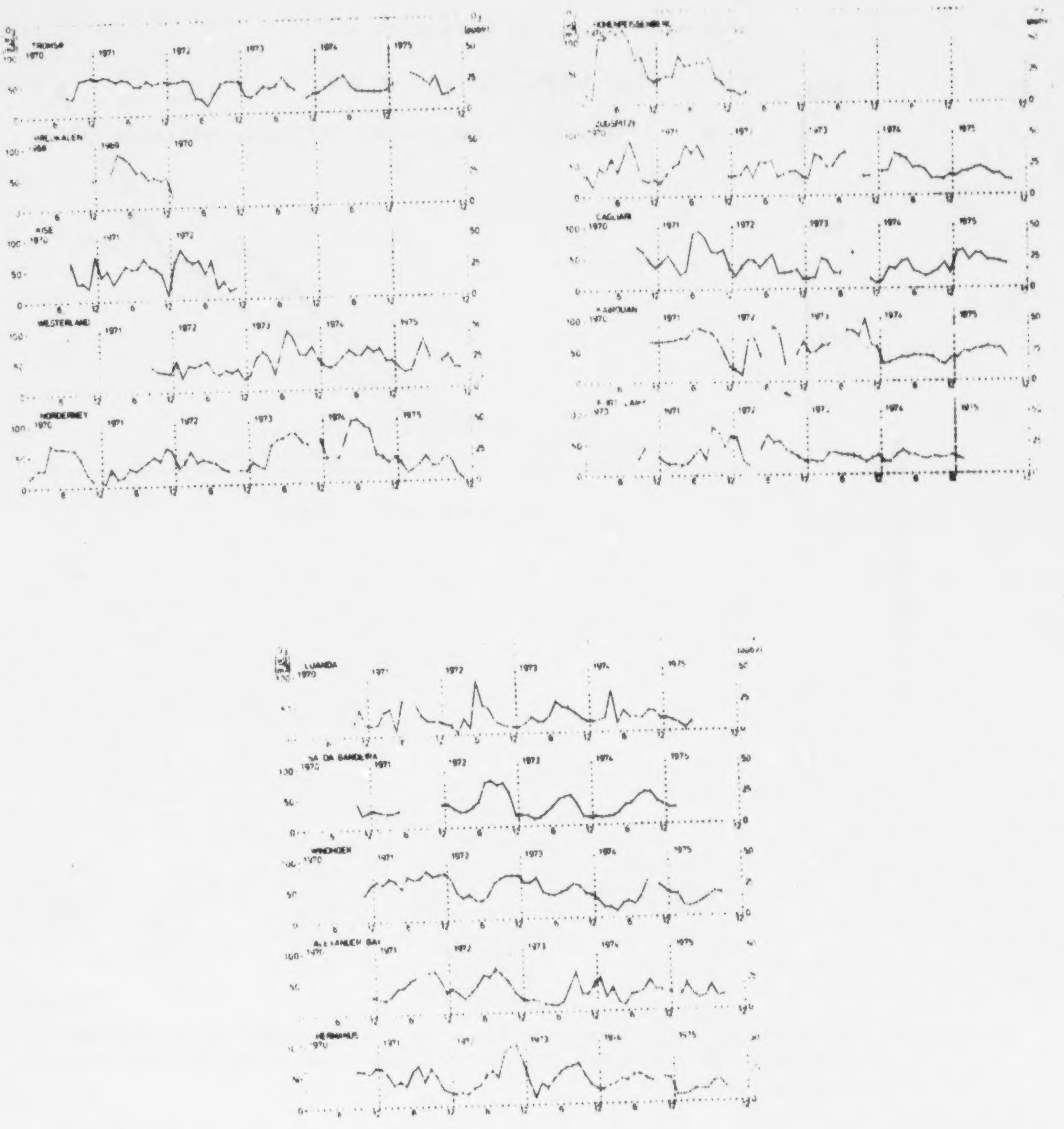
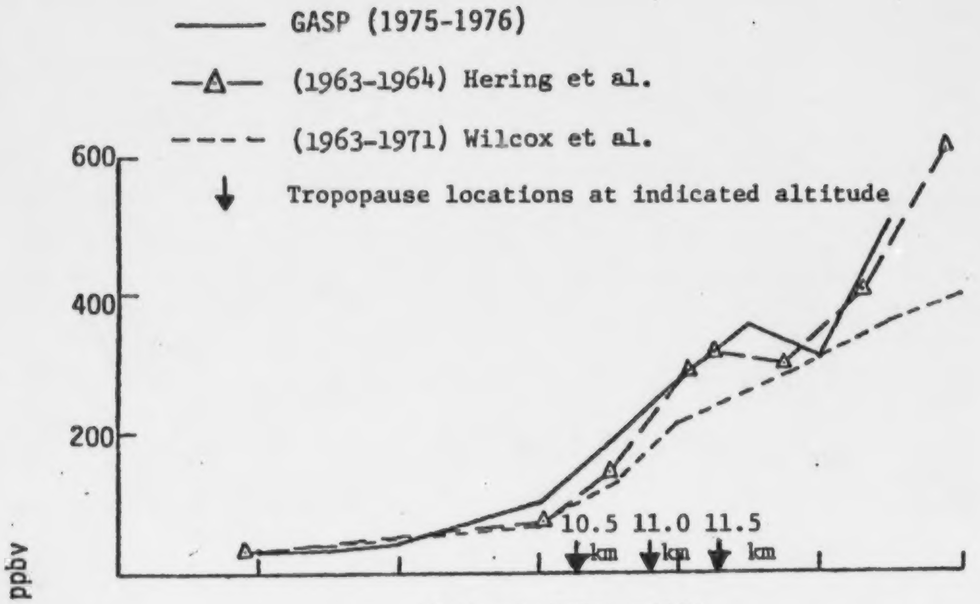
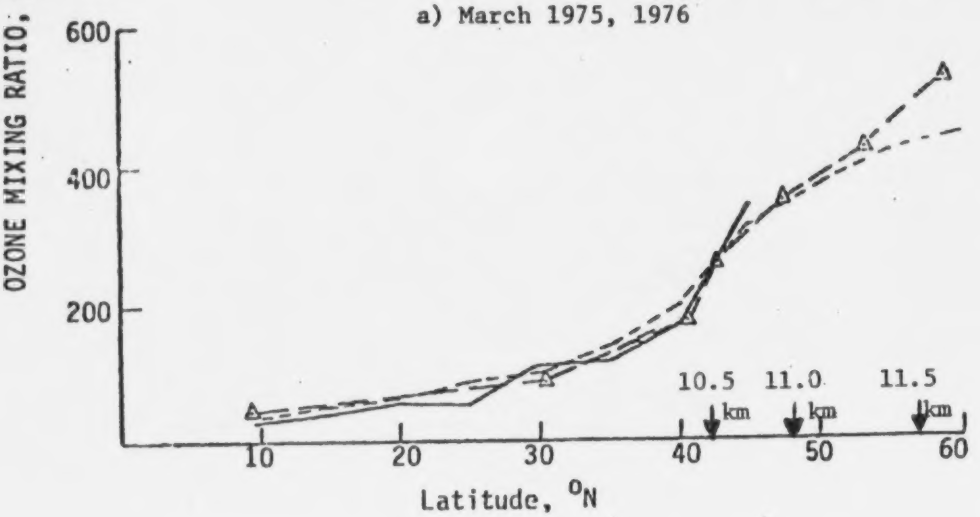


Figure 19. Monthly means of tropospheric ozone, derived from near surface registrations of project TROZ.

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P.G. Pruchniewicz. Contract No. FA 62/1 Deutsche Forschungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.



a) March 1975, 1976



b) May 1975

Figure 20. Variation of ozone mixing ratio with latitude for March and May. GASP Data for altitudes 10.5 - 11.5 km. Hering and Wilcox Data interpolated to 11 km.

Source: Holdeman, J.D. and F.M. Humenik: "NASA-GASP Data Report for Tape VL0005, NASA TMX-73608, Lewis Res. Center, Cleveland, OH, 32 pp. Feb. 1977.

Wilcox, R.W., G.D. Nastrom and A.D. Belmont: "Periodic analysis of total ozone and its vertical distribution," (RR-3, Control Data Corp.; NAS2-7807), NASA CR-137737 (1975).

Hering, W.S. and T.R. Borden: "Mean distributions of ozone density over North America, 1963-1964," AFCRL-65-913, Air Force Cambridge Research Labs. (AD-629989) (1965).

TABLE 4. AVERAGE MEAN a_1, AMPLITUDE a_2 AND PHASE a_3, OF ANNUAL WAVE AND THEIR MEAN STATISTICAL ERROR

Station	mean a_1 [$\mu g/m^3$]	amplitude a_2 [$\mu g/m^3$]	phase a_3 of annual maximum	a_2/a_1
Tromsö	40.4±3.3	6.2±4.9	May 7 ± 52 days	0.15
Bredkälen	45.7±11.4	13.8	April 20	0.30
Kise	44.8±0.2	12.5±10.0	May 15 ± 53 days	0.28
Westerland	47.1±9.8	10.3±3.0	July 1 ± 17 days	0.22
Norderney	41.9±15.4	15.7±6.5	July 3 ± 47 days	0.35
Lindau	34.4±13.3	11.7±5.1	June 6 ± 27 days	0.34
Hohenpeissenberg	64.8±16.5	34.4±8.8	June 22 ± 17 days	0.53
Zugspitze	45.1±5.4	15.2±4.7	June 23 ± 19 days	0.34
Cagliari	41.0±14.2	8.0±6.0	June 25 ± 48 days	0.20
Kairouan	56.1±15.6	14.3±3.2	July 11 ± 15 days	0.25
Fort-Lamy	33.4±6.0	6.9±5.0	June 15 ± 50 days	0.21
Luanda	28.8±3.0	12.6±3.3	July 14 ± 16 days	0.44
Sa da Bandeira	34.1±10.4	20.3±2.5	Sept. 2 ± 8 days	0.59
Windhoek	50.6±14.6	11.7±3.7	Oct. 20 ± 17 days	0.23
Alexander Bay	36.8±9.6	13.6±4.4	Sept. 15 ± 18 days	0.37
Hermanus	44.3±6.1	14.6±6.0	Sept. 3± 24 days	0.33

Source: Final Report on Project "Tropospharisches Ozon", P. Fabian and P.G. Pruchniewicz. Contract No. FA 62/1 Deutsche Forschungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

during May/June in low northern latitudes. In the southern tropics, a very strong phase variation with latitude is observed.

Using the extensive measurement records from the meridional network (Table 4), Fabian and Pruchniewicz (16) have calculated mean injection rates for ozone as function of latitude following the analytical concept derived by Junge (Equations 4 through 11). The unknown parameter C_o was obtained experimentally. Disregarding ozone destruction within the troposphere and assuming that ozone is decomposed at the surface, the ozone destruction rate F can be written as:

$$F + \varepsilon \cdot q \, [O_3]_o \qquad \text{(Eq. 12)}$$

where : surface parameter $o < \varepsilon \leq 1$ (depends on the conditions of the boundary layer, such as horizontal wind velocity and roughness length)

$[O_3]_o$: ozone concentration near the surface

q: specific ozone destruction rate of the particular surface type

q(sea surface) = 0.1 $cm \cdot s^{-1}$ (28)

q(land surface) = 1.0 $cm \cdot s^{-1}$ (29)

q(ice and snow) = 0.02 $cm \cdot s^{-1}$ (30)

From Equations 12 and 5 follows $\tau_t = C_o^{-1}$, i.e., the tropospheric residence time for ozone as function of latitude (see Figure 21).

The final results of Fabian and Pruchniewicz's ozone injection and surface destruction rates are shown in Table 5. Their values are very close to those obtained by

Danielsen: 7×10^{10} molecules$\cdot cm^{-2} \cdot s^{-1}$ (from analysis of tropopause folding events, cyclonic activity)

and Nastrom: 7.8×10^{10} molecules$\cdot cm^{-2} \cdot s^{-1}$ (from analysis of GASP data)

However, the two investigators used very different experimental approaches and assumptions in arriving at the above quoted stratospheric-tropospheric ozone fluxes.

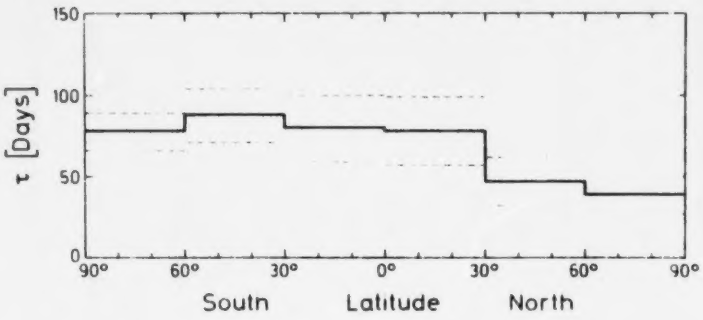


Figure 21. Mean residence time of ozone in the troposphere assuming destruction at the surface to be the only sink. The uncertainty range is due to uncertainties and variation range of wind velocity and roughness length (see Fabian and Junge [1970]).

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P.G. Pruchniewicz. Contract No. FA 62/1 Deutsche Forschungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

All the evidence accumulated so far on the original of the tropospheric ozone supports the "classical" concept of ozone intrusion from the stratosphere and destruction at or near the earth's surface as being the dominant source and sink for the tropospheric ozone. A substantial net production of ozone in the unperturbed troposphere due to photochemical processes involving the NO_x-H_2O-CH_4-O_2-O_3-system (without anthropogenic contributions) (31,32) is incompatible with representative tropospheric ozone measurements and budget calculations, and radio nuclide measurements, but the existence of this chemical process cannot be ruled out.

As was shown earlier (see Figure 16), simultaneous measurements of ozone and radioactive fallout (Sr^{90}) at a clean air station reveal a similar secular pattern except that there exists a phase shift difference (i.e., tropospheric lifetimes) for the two trace substances due to different removal processes. Reiter et al. (33) found a statistically significant correlation coefficient of 0.55 for the ozone/Be^7 and of 0.45 for the ozone/fallout pair of variates.

TABLE 5. CALCULATION OF GLOBAL SINK

		Southern hemisphere		Northern hemisphere	
Latitude	(10^{17} cm^2) area	mean injection (10^{10} mol/cm^2sec)	ozone sink (10^{27} mol/sec)	mean injection (10^{10} mol/cm^2sec)	ozone sink (10^{27} mol/sec)
$0^\circ ... 10^\circ$	4.450	4.0	17.799	4.0	17.799
$10^\circ ... 20^\circ$	4.298	4.4	18.912	5.35	22.995
$20^\circ ... 30^\circ$	4.033	5.7	22.987	6.8	27.423
$30^\circ ... 40^\circ$	3.645	4.8	17.496	7.95	28.978
$40^\circ ... 50^\circ$	3.146	4.4	13.844	8.7	27.374
$50^\circ ... 60^\circ$	2.552	3.0	7.657	8.05	20.546
$60^\circ ... 70^\circ$	1.881	2.5	4.701	6.9	12.976
$70^\circ ... 80^\circ$	1.152	3.55	4.088	6.9	7.947
$80^\circ ... 90^\circ$	0.388	3.55	1.377	6.9	2.676
		total S 10.9×10^{28} mol/sec		total N 18.9×10^{28} mol/sec	

Source: Final Report on Project "Tropospharisches Ozon," P. Fabian and P. G. Pruchniewicz. Contract No. FA 62/1 Deutsche Forchungsgameinschaft, Max-Planck-Institut Fur Aeronomie. MPAE-W-100-76-21.

With the available test volume of 290 pairs of variates (clean air station at Zugspitze, Germany during 1973-74), the highest accidental value of the correlation coefficient would be 0.178. Since Be^7 is a unique tracer of stratospheric origin, the "background ozone" observed at this station should have originated predominantly in the stratosphere.

The representative annual mean concentration of ozone for the unperturbed ("remote") troposphere has been subject to considerable debate. Most "rural" stations show an ozone diurnal indicative of substantial ozone destruction during times of limited vertical exchange, or of local or regional photochemical synthesis involving anthropogenic precursor gases or a combination of both. Mountain stations such as Whiteface Mt. (1600m MSL), N.Y., (26) or Hurricane Ridge (1700m MSL), Olympic Mt., Washington, (23), located over 100 miles from significant pollution sources, are suitable for obtaining representative tropospheric ozone concentrations. For Whiteface Mt., the secular variation of ozone concentration (derived from the 1974 continuous ozone measurements) is described by

$$\chi = 30 + 10 \sin [2\pi(t - 0.29)] \text{ (ppbv)} \qquad (30 \text{ ppbv} = 64\ \mu g \cdot m^{-3}) \qquad \text{(Eq. 13)}$$

$$\left(t = \frac{1}{12} \text{ to } \frac{12}{12} \text{ representing Jan.-Dec.}\right)$$

The annual mean of 64 $\mu g \cdot m^{-3}$ compares well with the mountain stations Hohenpeissenberg, Germany and Zugspitze, for which values of 64.8 and 45 $\mu g \cdot m^{-3}$ respectively have been reported (see Table 4). The diurnal variation of ozone at Whiteface Mt. is 12%. (The daily maximum occurs at 22:00 on an annual basis, as is to be expected from a mountain station.)

On the basis of a few stations with long-term continuous ozone measurements free of local or regional anthropogenic emissions (including ozone precursor gases), a range of χ(annual mean) = $30 \pm {}^{5}_{8}$ ppbv constitute a representative tropospheric ozone level for 35° to 50° N latitude. Note, however, that the tropospheric background level increases up to $\sim$40 ppbv during spring and early summer and declines to $\sim$20 ppbv in the late winter due to the seasonal variation in stratospheric injection rate.

Transport of ozone from the stratospheric source region to the ground is an integral part of the "classical" ozone cycle. The transport across the tropopause barrier occurs, for example, during cyclonic activity (30°-50° N latitude) through tropopause folds (see Figure 11). The ozone extruded in the folded tropopause, therefore, has the potential of occasionally causing elevated regional ground-level ozone concentration. To what extent it will exceed the seasonal or annual mean of the tropospheric background ozone concentration depends upon the dilution caused by mixing during the air's descent. Measurements of radioactivity made in Project Springfield (12) show that the dilution is concentrated along both the upper and lower boundaries, i.e., the ozone-rich zone or layer is maintained by a convergent inflow normal to the boundaries which counteracts the turbulent diffusion. In the center the dilution is usually less than a factor of 5. Therefore, if the layer descends close to the ground, ozone concentration of the order of 0.26 $\mu g \cdot g^{-1}$ (1.3×10^{-6} $g \cdot g^{-1}$) from Equation 3 divided by dilution factor 5), or 150 ppbv, are conceivable. The ozone-rich surface pattern is strongly asymmetrical due to the narrowness of the folded structure and the strong deformations in the descending air. Some local regions may be influenced by this ozone-rich layer for just 2 or 3 hours, others for 1 to 3 days. There is no meteorological reason that the intruded ozone-rich layers must descend to the ground for each and every tropopause folding event. The cyclonic index of 22.5 per year (11) for the contiguous United States (each cyclonic event lasting up to 4 days and associated with at least one tropopause folding event somewhere over the United States) appears to be sufficiently large so that excessively high regional ozone ground-level concentrations associated with baroclinic disturbances would be a common phenomena ("stratospheric ozone episodes") - if indeed it would be associated with each event.

The frequency distribution of ozone concentration at Whiteface Mt. shows for the year 1974 (see Figure 22):

- Total number of hourly ozone averages (978 hours of missing data)	7782 hours
- Number of hourly ozone averages exceeding 80 ppbv	69 hours

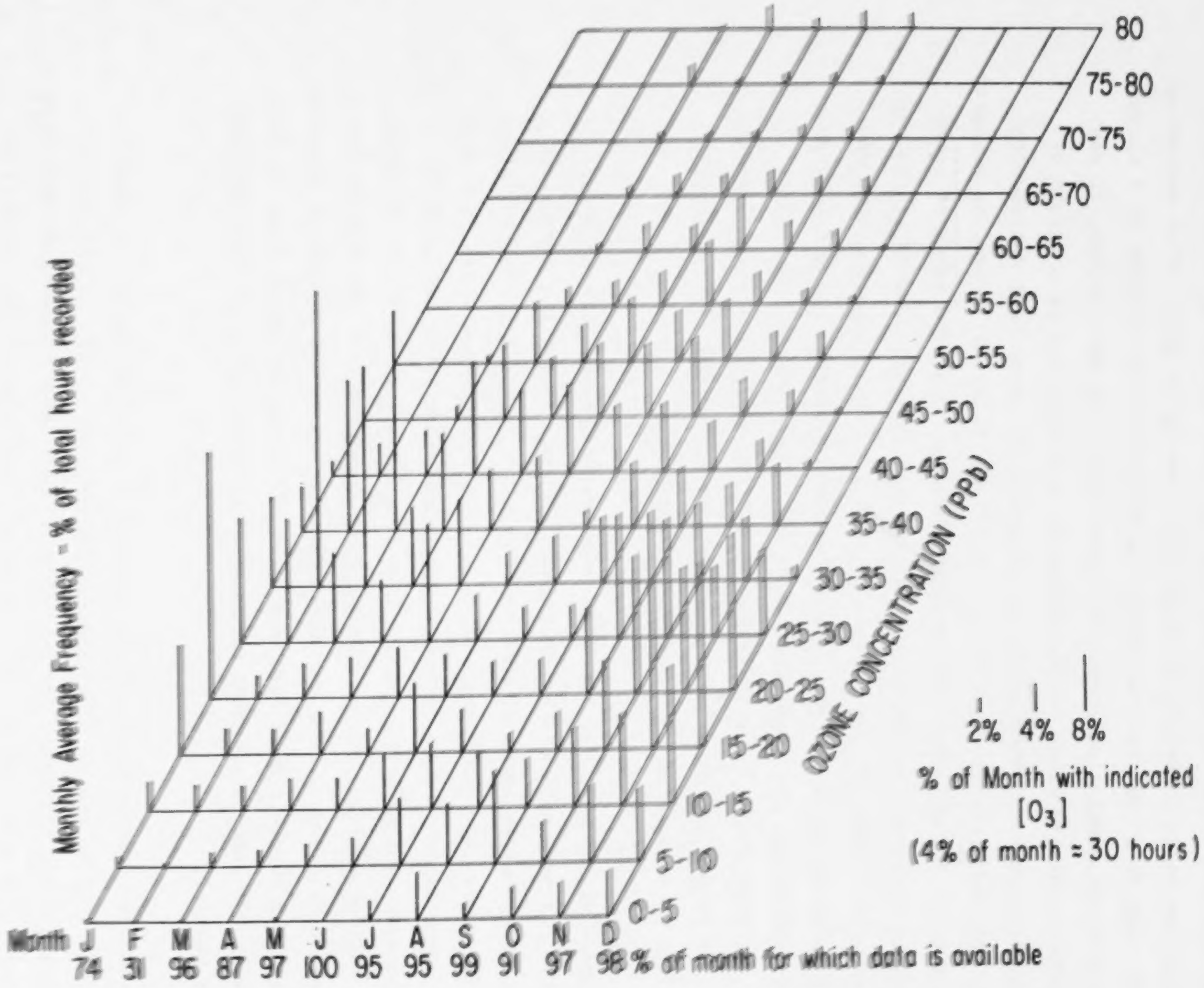


Figure 22. Frequency distribution of ozone concentration at Whiteface Mt. during 1974.

Source: Unpublished data from ASRC Whiteface Mt. Field Station. J. Kadlecek, V. Mohnen.

This statistic shows that in only 0.9% did the tropospheric ozone concentration within the clean planetary boundary layer exceed 80 ppbv. This percentage figure may vary from year to year since the meteorological pattern at a measuring site will not remain identical year after year. To what degree, if any, the observed excessive ozone concentration at Whiteface Mt. is a result of long-range transport of ozone and/or ozone precursor gases from metropolitan complexes (Chicago/Detroit, Boston, New York City, Montreal) cannot be assessed with any degree of certainty. It is shown, however, that the trend of ozone and the trend of potential temperature at the 850 mb level (see Figure 23) up to 250 mbs (see Figure 24) are alike. This very strongly suggests that the source of ozone is aloft, as does the night-peaking diurnal variation of mean ozone concentrations, and that ozone is brought down with the descending air masses. The case study for Whiteface Mt. covering the period July 21-August 1, 1975 (see Figure 24) showed hourly ozone concentrations in excess of 80 ppbv on July 31 associated with descending air masses.

Reiter (34) has examined the AFCRL ozonesonde network data from 1962 through 1965, a data base of some 1500 observations. From this sample, only 2% of the soundings exceeded 80 ppbv at ground level. Reiter chose to eliminate 28 of these cases as being suspect of tropospheric sources. This then places a lower limit of 0.2% on the 80 ppbv exceedance level, which is in reasonable agreement with the results from Whiteface Mt. It should be noted, however, that ground-level ozone concentrations deduced from ozonesondes are not representative means. The overwhelming majority of the ozonesonde ascents that Hering and Borden report were made close to 12:00 Universal time, or just after dawn local time, when ozone concentrations below the planetary boundary layer are minimal.

Reiter (34) also examined hourly ozone data from the Zugspitze, Germany, study for the period August 1973 through February 1976. Of the 529 days of observations, ozone mixing ratios exceeding 80 ppbv were encountered only 0.2% of the time. For these two events, isentropic back trajectories identified the ozone source in the lower stratosphere.

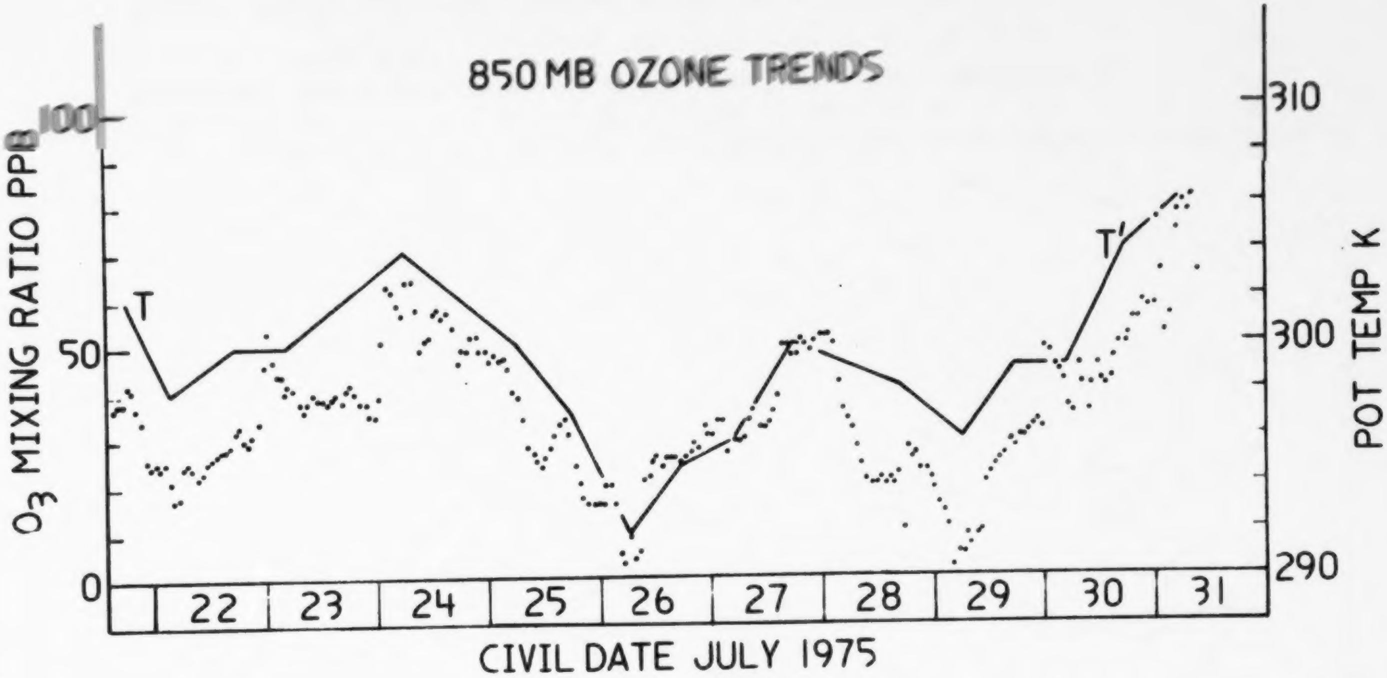


Figure 23. Ozone trend and potential temperature trend (850 MB) at Whiteface Mt.

Source: "Ozone Measurement and Meteorological Analysis of Tropopause Folding," V. Mohnen, A. Hogan, E. Danielsen, P. Coffey. Paper presented at International Conference on Photochemical Oxidant Pollution and Its Control, Raleigh, N.C., Sept. 12-17, 1976.

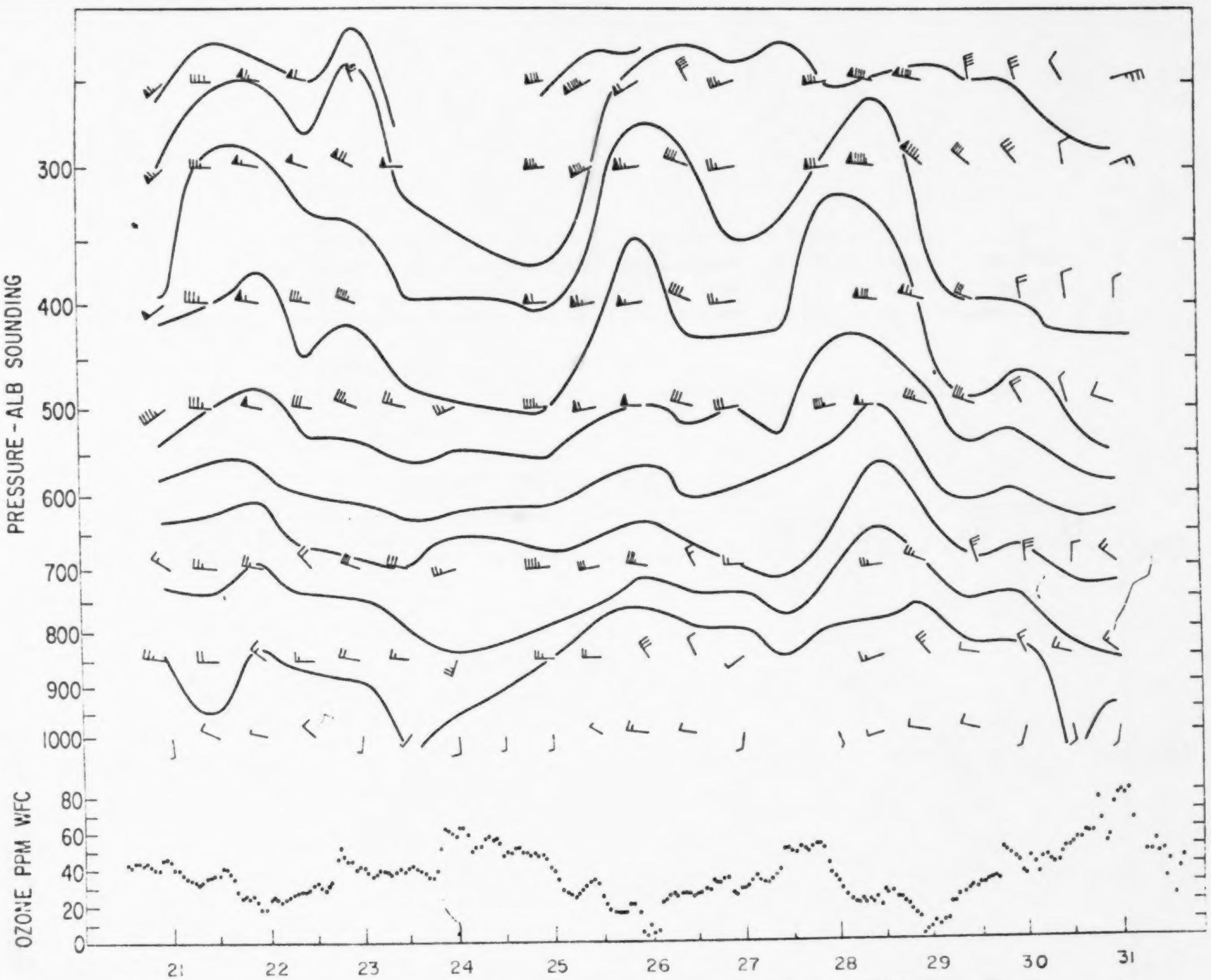


Figure 24. Isentropic analysis and ozone concentration - Whiteface Mt. - July 1975.

Source: "Ozone Measurement and Meteorological Analysis of Tropopause Folding," V. Mohnen, A. Hogan, E. Danielsen, P. Coffey. Paper presented at International Conference on Photochemical Oxidant Pollution and Its Control, Raleigh, N.C., Sept. 12-17, 1976.

Carney (35) examined also the ozonesonde data from eight stations within the contiguous United States in the network operated by the Air Force Cambridge Research Laboratory (36). Ozonagrams from April 3, 1963, to December 12, 1965, were used for Carney's study. Carney tested Reiter's (37) hypothesis describing a transport mechanism that correlated high low-level ozone amounts at mid-latitudes to the seasonal fluctuations of an "ozone reservoir" in the lower stratosphere and to synoptic scale transport in the troposphere. Carney assumes that vertical distribution of ozone can be used to discern the principal source of low-level ozone. For convenience, a level of significance was chosen to be an ozone mixing ratio of 0.10 $\mu g \cdot g^{-1}$ (or 0.06 ppbv at 20°C). Soundings were considered critical when the mixing ratio exceeded this level below 500 mb. The premise is that if ozone is transported downward from above the selected 500 mb level, the sounding should show no gradient or a positive ozone concentration gradient with ascent. (This assumes a continuous downward transport instead of massive short-term transports that may occur in the vicinity of large convective cells or squall lines.) Carney classified these ozone soundings as "transport type." Distributions that suggest a possible low-level source of ozone were referred to as "photochemical type." The results of Carney's investigation follow.

Critical soundings at Point Mugu, California generally had steep gradients near the surface. Lea (38) has demonstrated a correlation between ozone maxima and easterly winds bringing air from the Los Angeles basin to the launch site. Otherwise the overwhelming majority of the critical soundings were of the "transport type," with constant or increasing mixing ratios with height. It appears therefore that most high tropospheric ozone concentrations ($>0.10\ \mu g \cdot g^{-1}$ below 500 mb) were largely the result of transport from aloft, conceivably the stratosphere.

The frequency of stratospheric ozone intrusion is sporadic due to the sporadic occurrence of cyclonic events or other exchange mechanisms. After injection, the ozone-rich layers or zones disperse in time, depending on the atmospheric stability structure. It is, therefore, not surprising to occasionally find ozone layers of variable thickness imbedded in the troposphere, as has been reported in literature (see, for example, reference 39). It is

TABLE 6. CLASSIFICATION OF CRITICAL OZONAGRAMS BY VERTICAL DISTRIBUTIONS (> 0.10 $\mu g \cdot g^{-1}$ below 500 mb)

	Total Soundings	A	Percent of Critical Soundings*	B	Percent of Total Soundings*	C	D
Albuquerque, NM	200	17	8.5%	13	6.5%	4	0
Bedford, MA	185	34	18.4%	12	9.2%	13	4
Fort Collins, CO	152	21	13.8%	18	11.8%	1	2
Green Bay, WI	53	4	7.5%	4	7.5%	0	0
Madison, WI	28	11	39.3%	6	21.4%	3	2
Pt. Mugu, CA	18	6	33.3%	0	0.0%	6	0
Seattle, WA	139	29	20.9%	21	15.1%	2	6
Tallahassee, FL	129	33	25.6%	23	17.8%	5	5
Totals	904	155 (100%)	17.1%	102 (65.8%)	11.3%	34 (21.9%)	19 (12.3%)

A - Number of critical soundings

B - Number of "transport" soundings

C - Number of "photochemical" soundings

D - Number of unclassified soundings

* Total soundings equals 100%.

Source: Carney, T.B. Evidence of the Role of Stratospheric Transport in the Distribution of Tropospheric Ozone. Ozone/Oxidants - Interactions with the Total Environment. APCA Specialty Conference (Southwest Section), Proceedings. Air Pollution Control Association, Pittsburgh, Pa., 1976. pp. 234-241.

also not surprising to find the ozone mixing ratio in the chemically unperturbed troposphere fluctuating from day to day. The concept of a well mixed tropospheric ozone content can only be considered as a first rough approximation. Prunchniewicz (40) has analyzed the ozonagrams obtained from 1963-1966 by Dutsch (41). He compared the ozone mixing ratios at the 400 mb and 500 mb layer for a certain day T with the corresponding value for the previous day T-1 or T-2. His results (shown in Figures 25 and 26) demonstrate the great variability of the ozone in the mid-troposphere, although the intrusion (tropopause) and destruction region (below planetary boundary layer) are quite some distances above and below the selected observation layer. The mean ozone mixing ratio in that layer was found to be 0.08 $\mu g \cdot g^{-1}$ (400-500 mb), with a mean deviation of 50% for the (T, T-1) and 25% for the (T, T2) data pairs. Pruchniewicz (40) attempted, furthermore, to correlate the relative changes of ozone mixing ratios at the 300 and 500 mb layer with those at the 200 mb layer ("stratospheric ozone reservoir"). He found correlation coefficients between 0.05 and 0.35, i.e., there exists only weak correlation between the stratospheric and tropospheric ozone content within a vertical column above a fixed geographic location. This means that the ozone measured in the mid-troposphere did not, in most cases, originate from the stratospheric reservoir directly above, but was injected into the troposphere at any point "upwind." The importance of tropospheric ozone transport and mixing processes have thus been clearly demonstrated.

All ground-level ozone observations exhibit a definite "spring rise phenomena" which is attributed to the increased stratospheric-tropospheric transport of ozone-rich air (Figures 2, 3, 13, 16, and 19). The magnitude and time of the year of the resulting primary ozone maximum, as shown earlier, depends on the geogrpahic latitude of the ground-level measuring site. There are indications of secondary ozone maxima occurring in early summer and/or broad maxima extending from April into August. Fabian and Pruchniewicz (16) have shown through harmonic analysis of the annual variation of ozone observed in the meridional network (Figure 19) that only the annual wave is statistically significant. Higher harmonies are insignificant, without exceptions, for all stations in his network.

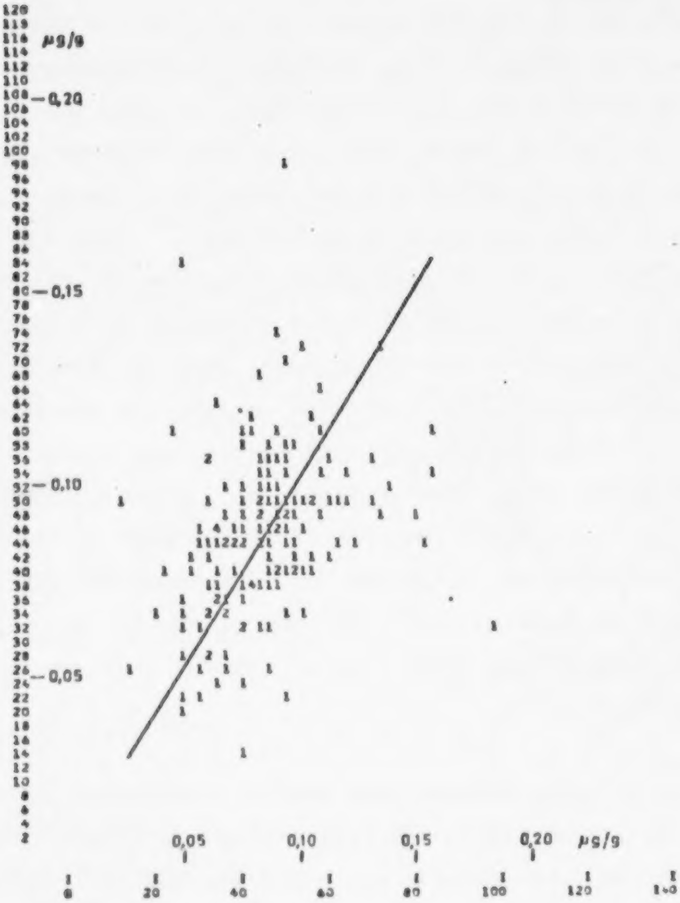


Figure 25. Correlation of tropospheric ozone mixing ratio for a day T with mixing ratio for day T-1. Each data point consists of a pair of ozone mixing ratios for day T and T-1. This graph is made up of a total of 161 ascents, with ozone mixing ratios from the 400 and 500 mb layer over Boulder, Colorado (ozonesondes by Dutsch). Seven data pairs (4.35%) are in excess of 0.15 $\mu g \cdot g^{-1}$.

Source: P.G. Pruchniewicz, "Uber ein Ozon-Registriergerat und Untersuchung der zeitlichen und raumlichen Variationen des Tropospharischen Ozons auf der Nordhalbkugel der Erde." Mitteilungen, Max-Planck-Institut fur Aeronomie, No. 42, 70 pp (1970). Springer-Verlag, Berlin-Heidelberg-New York.

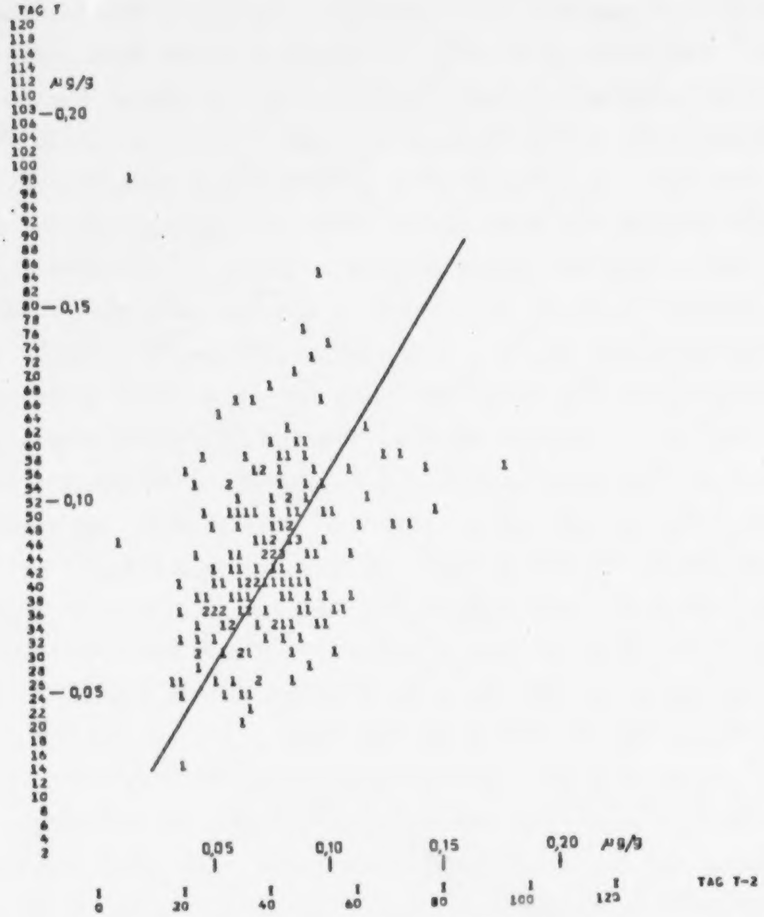
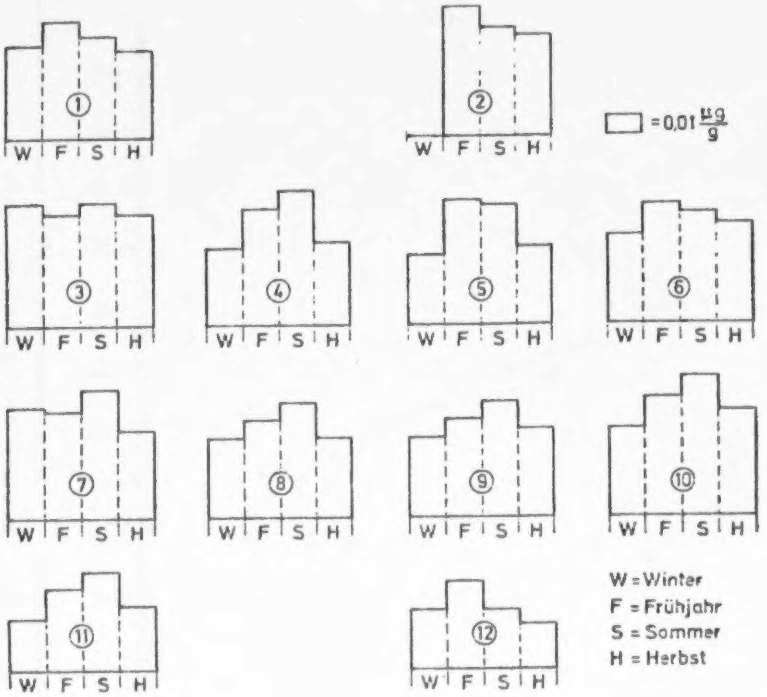


Figure 26. Correlation of tropospheric ozone mixing ratio for day T with mixing ratio for T-2. Each data point consists of a pair of ozone mixing ratios for day T and T-2. This graph is made up of a total of 174 ascents, with ozone mixing ratios from the 400 and 500 mb layer over Boulder, Colorado (ozonesondes by Dutsch). Five data points (2.9%) are in excess of 0.15 $\mu g \cdot g^{-1}$.

Source: P.G. Pruchniewicz, "Uber ein Ozon-Registriergerat und Untersuchung der zeitlichen und raumlichen Variationen des Tropospharischen Ozons auf der Nordhalbkugel der Erde." Mitteilungen, Max-Planck-Institut fur Aeronomie, No. 42, 70 pp (1970). Springer-Verlag, Berlin-Heidelberg-New York.

Pruchniewicz (40) has reanalyzed the ozonesonde data of the AFCRL network (Figure 4) and calculated the mean ozone mixing ratio between 1 km and 9 km altitude for all 13 stations as a function of season. His results are shown in Figure 27. The averaged "total" tropospheric ozone does indicate a persistence of high tropospheric ozone values into the summer period. Falconer (42) has demonstrated on the basis of available GASP data (1975/76) that this biomodality for the tropospheric ozone concentration does also exist at levels just below the troposphere (see Figure 28). His explanation for the statistically significant secondary ozone maximum is based on the fact that the tropopause rises rapidly in early summer within the latitude belt 30-60°N. Hence, previously stratospheric air (and "stratospheric" ozone) will be incorporated into the troposphere. The resulting ozone intrusion will eventually be transported down to the ground and give rise to increased ground-level ozone concentrations leading conceivably to a secondary ozone maximum and/or broadening effect of the primary spring maximum. On the basis of available data, one cannot exclude at this time that the tropospheric methane oxidation cycle could also contribute to and enhance the "delayed decline" of tropospheric ozone concentration from the spring maximum to the winter minimum. The observations of Falconer (42) (GASP data) presented in Figure 28 are, however, incompatible with a major ozone source strength located within the unperturbed troposphere. It is generally agreed that no net production of ozone occurs above 6 km altitude involving the methane oxidation cycle. Hence, meteorological exchange and transport processes (cyclonic activity and tropopause lifting) must again be mainly responsible for the observed ozone concentration. Further indication for the validity of the "meteorological" concept is seen in Figure 27. The ozonesonde data from Albrook (Balboa), located near the equator, show a spring maximum but no indications of a summer peak (note that there is no tropopause rise at low latitudes; see Figure 8, "Swan Island") although the solar intensity would favor highest photochemical activity.

Global mesoscale and microscale meteorology-climatology plays a dominant role in determining the daily, seasonal, and secular characteristics of the tropospheric ozone concentration.



1	Thule	76,5°N
2	Alaska	64,8°N
3	Fort Churchill	58,8°N
4	Goose Bay	53,8°N
5	Seattle Washington	47,4°N
6	Green Bay	44,5°N
7	Bedford	42,5°N
8	Ft. Collins/Colorado	40,6°N
9	Albuquerque/ New Mexico	35,0°N
10	Tallahasse/Florida	30,4°N
11	Grand Turk	21,5°N
12	Albrook (Balboa)	9,0°N

Figure 27. Secular variation of tropospheric ozone concentration over North America (µg/g). Mean ozone mixing ratio between 1 km and 9 km altitude extracted from ozonesonde data 1963, 1964, and 1965.

Source: P.G. Pruchniewicz, "Uber ein Ozon-Registriergerat und Untersuchung der zeitlichen und raumlichen Variationen des Tropospharischen Ozons auf der Nordhalbkugel der Erde." Mitteilungen, Max-Planck-Institut fur Aeronomie, No. 42, 70 pp (1970). Springer-Verlag, Berlin-Heidelberg-New York.

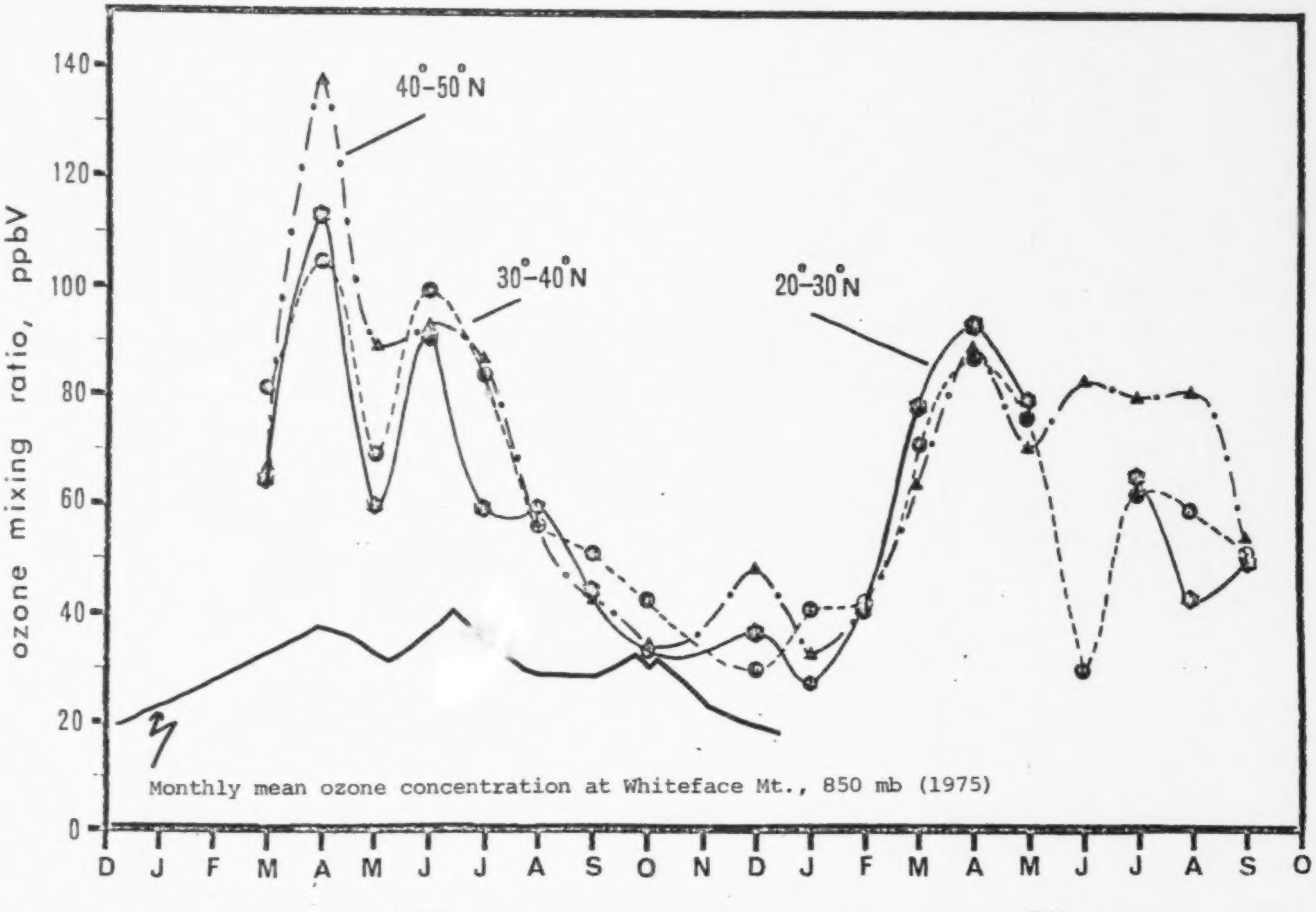


Figure 28. Mean, monthly ozone mixing ratios obtained in the upper troposphere by participating GASP airliners.

Source: P.D. Falconer: "The Global Atmospheric Sampling Program: The Prospects for Establishing a Tropospheric Ozone Budget from Commercial Aircraft Data." To be presented at the ASTM Conf. on Air Quality Meteorology and Atmospheric Ozone, 1-6 August 1977, Boulder, Colo.

As pointed out earlier, stratospheric ozone can occasionally reach the ground, causing excessively high concentration levels of regional extent. There are a few reports in the literature of those ozone episodes. Walker and Hathorn (3) described such a possible case for Texas, with ozone levels exceeding 80 ppb for several days (September 25 - October 1, 1975). Huffman et al. (25) reported on a high regional ozone incidence that occurred on February 24, 25, and 26, 1976. A typical tropopause folding event over the midwest was identified as the source of ozone.

There are no statistics available at this time for the frequency of occurrence of "stratospheric ozone episodes" of regional extent. They may be infrequent, but cannot be defined from commonly available surface ozone data, most of which is influenced by local or regional pollution.

SUMMARY

The ozone concentration in the unperturbed troposphere is governed mainly by stratospheric ozone intrusion and by ozone destruction at the surface and/or within the planetary boundary layer. The contributions of the various stratospheric-tropospheric transfer processes to the total amount of ozone transported into the troposphere are not yet well established. The resulting annual mean concentration representative for the unperturbed lower troposphere (near ground) is of the order of $30 \pm^{5}_{8}$ ppbv for the 30° - 50°N latitude belt. Ground-level ozone concentrations (hourly averages) exceeding 80 ppbv occur at a frequency of less than 1% on an annual basis. "Stratospheric ozone episodes" are rare events. A frequency of occurrence cannot be established at this time. The methane oxidation cycle does not constitute a dominant source of tropospheric ozone. It must be pointed out that considerably more research efforts are required to quantify the various meteorological and chemical processes governing the natural ozone cycle. The lack of long-term measurement series from ground-level stations representative for the unperturbed natural troposphere is a very serious limitation for refining our knowledge of the "natural ozone."

ACKNOWLEDGMENTS

The author is very grateful to Dr. Edwin Danielsen of the National Center for Atmospheric Research, and to Dr. Austin Hogan and Phillip Falconer of the Atmospheric Sciences Research Center for many clarifying discussions.

COMMENTS BY ELMAR REITER

In summary, I should like to say that Mohnen's paper is excellent. Its overall conclusions agree with those I have reached in my paper. There are, however, some internal inconsistencies in the use and interpretation of data which might, in a few places of his discussion, lead the reader to expect very high influxes of stratospheric ozone. My following discussion points out these inconsistencies. If Dr. Mohnen could reconsider the use of some of these values, all aspects of his paper could be brought into total agreement with his and my final conclusions.

In Mohnen's report a major difficulty exists on pp. 15-19. On p. 15 he quotes Danielsen's estimate of 4.3 x 10^{20}g/year (i.e., 95% to 100% of one hemispheric stratosphere) due to eddy transport. I don't know where this quotation comes from. It is not in the Danielsen paper referenced on p. 15. This number is either wrong, or attributed to the wrong transport processes. If one were to add to this eddy transport the other transport processes quoted in my report (see Table 1 of my report) one would end up with 179% of one hemispheric stratosphere exchanged per year. This would lead to a mean residence time (according to my Eq. 1) of 0.56 years or 6.7 months, which is clearly in disagreement with observed Sr^{90} residence times in the stratosphere.

The last paragraph on p. 16 in Mohnen's paper ascribes the discrepancy between Danielsen and myself to wrong inferences from just one case study. Actually, there were several such studies in good agreement with each other, and *my* value has been compared with a total stratospheric mass balance (see Table 1 in my report). To my knowledge this has not been done with Danielsen's number. Again I have to state, that I don't know how he derived his number.

The estimate of 80% mass exchange rate quoted on p. 18 of Mohnen's report, on the other hand, refers to the *total* outflow rate from the stratosphere (including effects of the mean meridional circulation) and is in reasonable agreement with my estimates (average of 89 and 73%, see p. 74 of my report). Mohnen apparently takes this correct estimate of *all* transport processes in support of the wrong statement of 90% due to *eddy* transports (p. 16 of his report).

On p. 20 there is another questionable use of data. Mohnen assumes an ozone mass mixing ratio in the lower stratosphere of 1.3×10^{-6}g/g. This value occurs at levels above the tropopause which usually are not involved *directly* in the intrusion processes (see for instance Mohnen's Figure 11 and my Figure 7). Very recent measurements, to be published by Mel Shapiro of NCAR, suggest that a value of 0.5 to 0.7×10^{-6}g/g would be a more appropriate O_3 mixing ratio to use in such ozone transfer estimates into the troposphere. Thus Mohnen's outflow rates are overestimated by a factor of 2. *Note:* The relatively low mean ozone concentration in the layers above the tropopause apparently comes about by the fact that tropospheric air is mixed into the stratosphere near jet streams. From Be^7 and P^{32} observations, E. Reiter, and R. Reiter et al., (33,43) have concluded that air in the lower stratosphere, to an appreciable extent, is of tropospheric origin.

The outflow rates computed by Mohnen, using Equations 2 and 3 are subject to the same overestimate of low-tropospheric O_3 concentrations. When all is considered (Mohnen, p. 25) the annual outflow rate should be of the order of 2×10^{14}g *or less;* 8×10^{14} g would be an overestimate by a considerable factor.

If the estimates of vertical velocity, $\overline{w}$, are to be extended over the whole hemisphere and not just in the jet-stream region, a value of 0.5 cm/sec is an overestimate by at least a factor of 2 (see my paper, p. 82).

On p. 46 the mass flux of 7×10^{10} molecules$\cdot$cm^{-2}sec^{-1} should be attributed to *all* processes, and not to eddy processes and tropopause folding alone.

A mean tropospheric background level of 30 ppb quoted on p. 49 agrees excellently with my estimates.

Mohnen's estimate (p. 52) of 0.9% of hours exceeding the Federal standard, does not disagree with my value of 0.2% of local exceedance probability, which refers to days during which the 1-hour standard is exceeded.

Last sentence in first paragraph on p. 52: Change to "...ozone concentrations in the lower part of the planetary boundary layer are minimal."

REVIEW AND ANALYSIS

Elmar R. Reiter

ABSTRACT

High ozone concentrations in rural areas far away from possible industrial sources have been blamed, at least in part, on stratospheric air intrusions into the troposphere. The assessment of the actual impact of such intrusions on ground-level ozone concentrations requires sophisticated analysis techniques which are not without difficulties. This paper explores various estimates of the impact of stratospheric ozone on ground-based ozone (O_3) concentration measurements. Measurements on mountain peaks have to be treated with special care because, due to local circulation systems and to mountain-generated turbulence, they could be contaminated by air masses of low-tropospheric origin, whereas the closest radiosonde ascent might not reveal such contamination. Circumstantial evidence is presented in this paper for a low-tropospheric "ozone climatology."

INTRODUCTION

The search for the origin of high oxidant concentrations frequently encountered in rural areas still is faced with conflicting evidence. Whereas there is no doubt that photochemical reactions of certain pollutants in the low troposphere, especially within the planetary boundary layer (into which most of the anthropogenic contaminants are emitted), play a major role in generating high oxidant concentrations observed close to the ground, a controversy still exists about the impact of stratospheric air intrusions on low-tropospheric ozone "background" and "peak" concentration values (1).

This paper tries to provide an assessment of the processes involved in generating high ozone concentrations of possible stratospheric origin near the ground. It weighs some of the conflicting observational evidence, points out possible sources of error and suggests approaches for additional investigations.

THE STRATOSPHERIC RESERVOIR

Photochemical production and destruction mechanisms of O_3 in the stratosphere have come under close scrutiny during the Climatic Impact Assessment Program (CIAP) sponsored by the U.S. Department of Transportation (33). The effects of anthropogenic halocarbons have been included recently in the long list of possible photochemical reactions (see for example, reference 44), and the complexity of chemical interactions in the stratosphere recognized as having possible effects on the O_3 reservoir is increasing steadily. Interactions of O_3 with NO_x are still considered as being of major importance in controlling the stratospheric O_3 distribution, together with the "Chapman mechanism" of direct production and destruction of O_3 by UV absorption. Recent studies (45) have addressed themselves to cataclysmic increases of stratospheric NO_x from a nuclear holocast, but also to the more subtle effects of volcanic eruptions.

The magnitude of long-term anthropogenic effects on the stratospheric ozone reservoir is still very much under dispute. It could amount to anywhere from 5 to 20 percent. A long-term variability of similar magnitude can be attributed to changes in the effectivenss of stratospheric transport processes. The variability of these transport processes is tied to climatic variations. Colder climates would show significantly lower stratospheric ozone concentrations in middle and high latitudes than would warmer climates (46).

In an assessment of the effects of stratospheric ozone on low-tropospheric oxidant concentrations, can the long-term (secular) variability of the stratospheric ozone reservoir be ignored? A number of stations (as exemplified by Arosa, Switzerland) have shown a gradual increase in total atmospheric ozone, especially during the spring months of recent years. According to

Figure 1 the annual *spring peak* of total ozone over Arosa increased by approximately 20 percent between 1967 and 1970 (47). Angell and Korshover (48) pursued the problem of long-term variability of global ozone in more detail. Figure 2 depicts this variability in several geographic sectors, together with a plot of smoothed sunspot numbers. It is very tempting to conclude that the sharp increase in total ozone during the late 1960's coincided with an increase in sunspot activity, and the decrease in O_3 observed during the early seventies, likewise, parallels a decrease in sunspot numbers. There is some doubt about the accuracy of the Russian filter ozonometer. If one considers, therefore, only the European and American measurements, an amplitude of the secular variability of total ozone of about 10 percent appears to be a reasonable assumption.

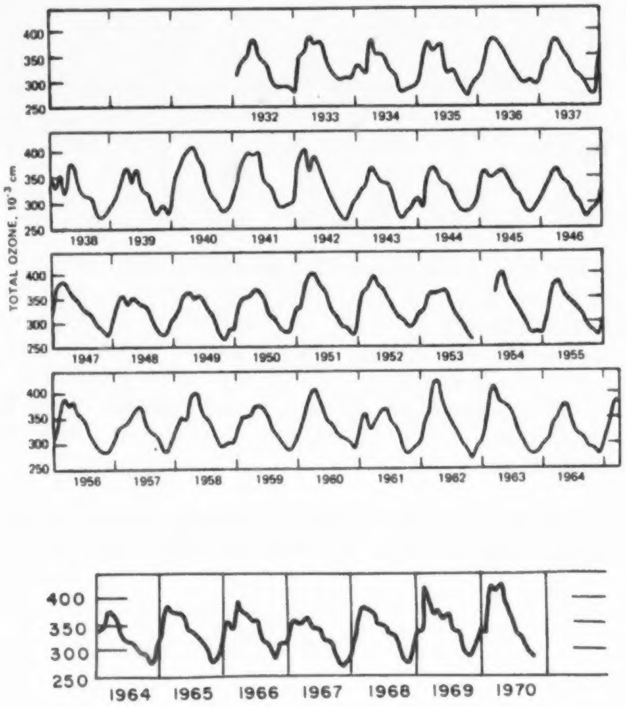


Figure 1. Monthly mean total ozone amounts at Arosa, Switzerland (46.5°N, 9.4°E). [Top part of diagram from J.M. Wallace and R.E. Newell, Quarterly Journal of the Royal Meteorological Society, 92; 487 (1966); bottom part of diagram: data courtesy of Dr. J. London.]

Source: Reiter, E.R., and B.C. MacDonald. Quasi-Biennial Variations in the Wintertime Circulations of High Latitudes. Arch. Meteorol. Geophys. Bioklim., Series A, 22(1):145-167, 1973.

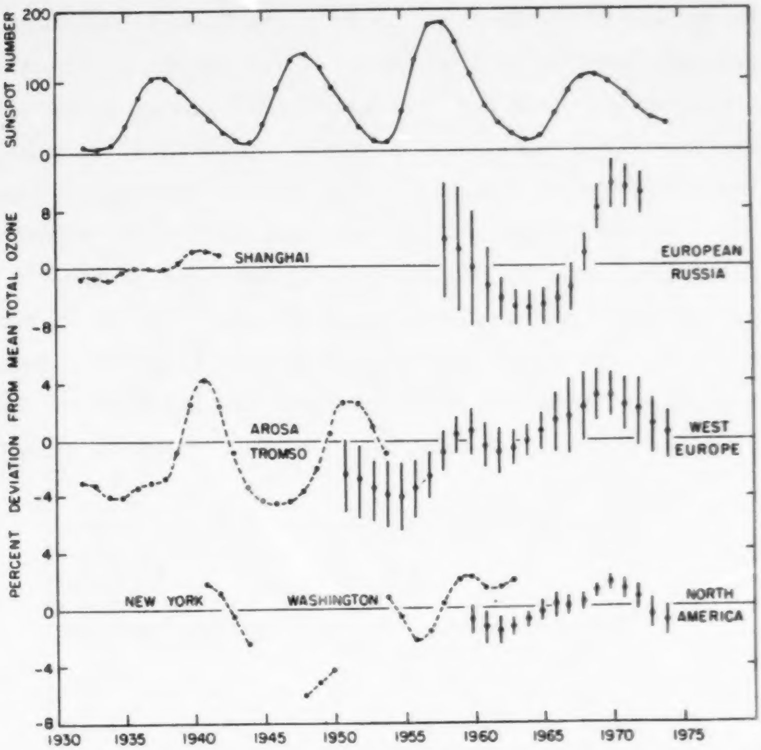


Figure 2. Comparison of the smoothed sunspot number with the total-ozone variation in regions with the longest records and most stations. The data at right include an extension in time of the West European and North American traces based on recent British and United States data. The dashed lines at left indicate the total-ozone values for individual stations, including data recently collected for Washington, D.C. Note the change in scale for European Russia and Shanghai.

Source: Angell, J.K., and J. Korshover. Global Analysis of Recent Total Ozone Fluctuations. Monthly Weather Review, 104(1):63-75, 1976.

Figure 3 indicates that the long-term trend is most strongly expressed in winter and spring. These are the seasons during which the stratospheric ozone reservoir is "filled to capacity" (Figure 4). The *seasonal* variability of O_3 in middle and high latitudes, according to Dütsch (49) amounts to approximately 38 percent.

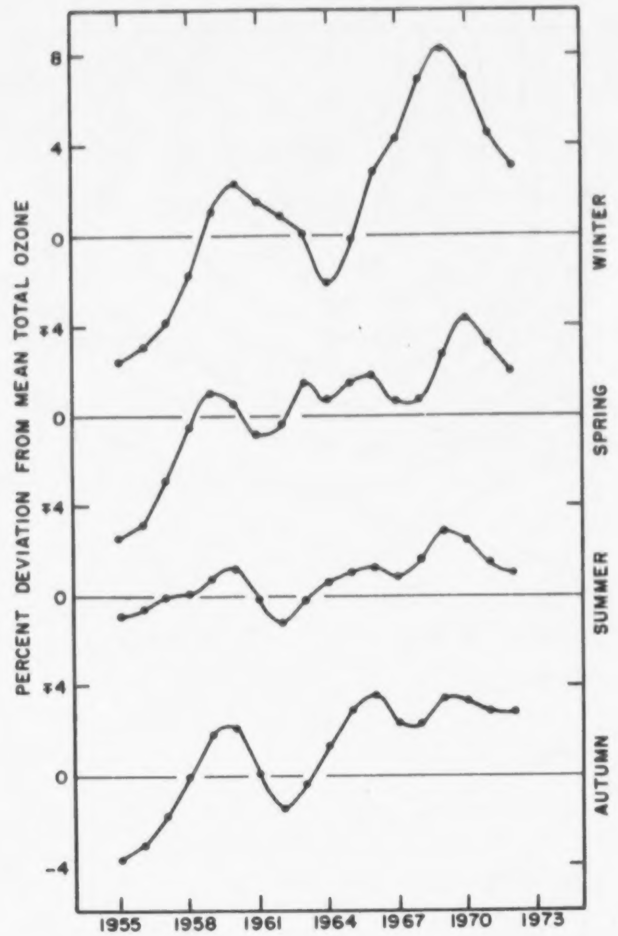


Figure 3. Temporal variation in total ozone in West Europe by season. A 1-2-1 smoothing has been applied to the successive yearly values for each season.

Source: Angell, J.K., and J. Korshover. Global Analysis of Recent Total Ozone Fluctuations. Monthly Weather Review, 104(1):63-75, 1976.

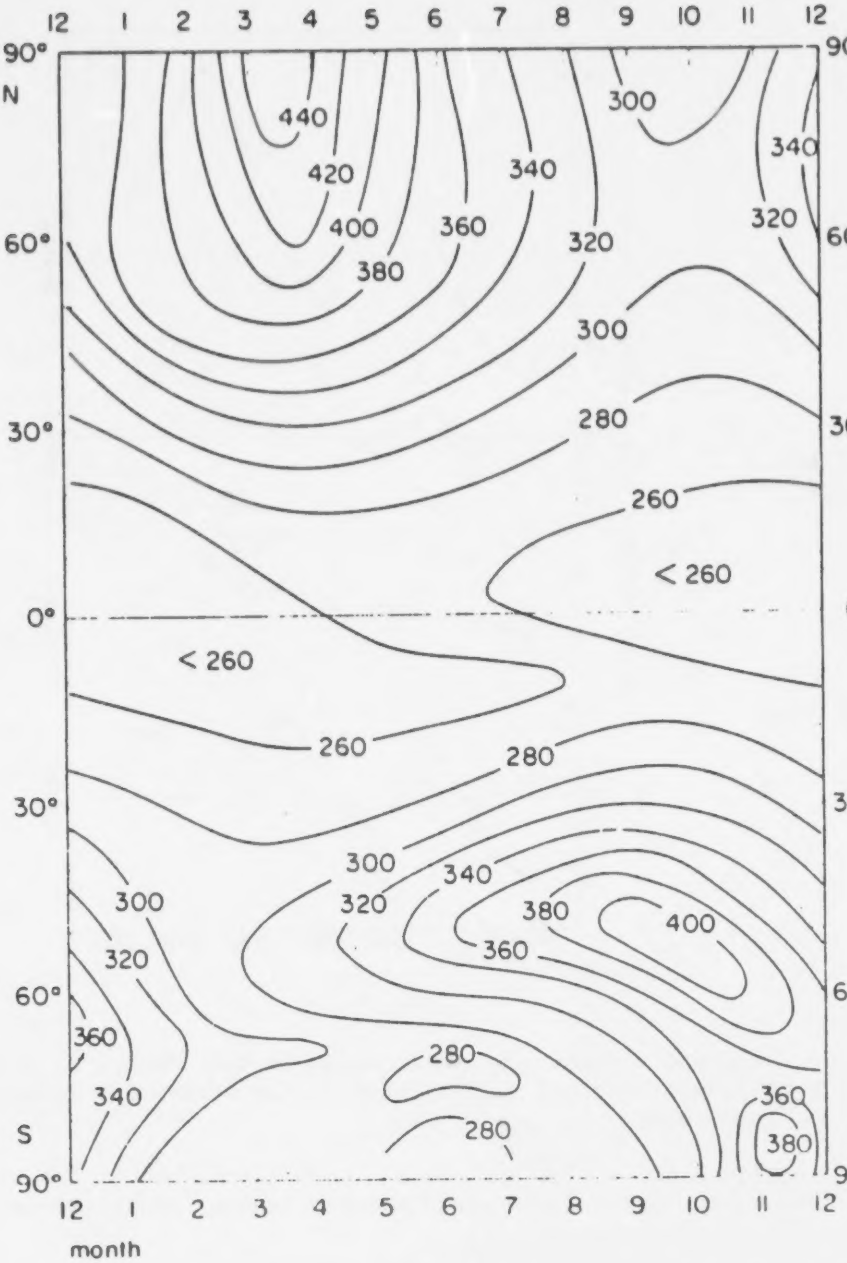


Figure 4. Worldwide total ozone as a function of season and latitude [From Dütsch (1971), based upon data by London (1963) and Sticksel (1970)]. The numbers are total amounts in the conventional units of 10^{-3} atm-cm STP.

Source: Reiter, R., H.J. Kanter, R. Sladkovic, and K. Potzl. Measurement of Airborne Radioactivity and Its Meteorological Application. Part V. Annual Report 1 April 1973 - 31 July 1974. Institut Fur Atmospharische Umweltforshung. ERDA Document No. NYO-3425-12. 1976.

In conclusion, we can state that the stratospheric reservoir of ozone is subject to a strong seasonal modulation (38%), with a weaker (10%) secular trend superimposed. The seasonal variation of stratospheric ozone certainly will have to be taken into account in an assessment of the impact of stratospheric ozone on ground-level oxidant concentrations. The effects of a secular trend of the magnitude indicated above can, perhaps, be ignored for the time being, because other processes described in the subsequent sections are beset with much larger "error bars" than 10 percent. If, however, anthropogenic effects on stratospheric ozone should increase its secular variability significantly beyond this value, the natural background of ground-level oxidants will have to be adjusted accordingly.

STRATOSPHERIC-TROPOSPHERIC TRANSPORT PROCESSES

The interchange of stratospheric and troposphere air masses proceeds by various mechanisms, each of which is characterized by short- and long-term variability with time. The following mean magnitudes of mass flux from a "box" encompassing one hemispheric stratosphere, in percent of the mass equivalent to that in this "box," have been estimated from evidence presented in the literature (for references see Reiter (7,50,51); Singh et al. (52)).

TABLE 1. ANNUAL MASS FLUX FROM STRATOSPHERE,
IN PERCENT OF MASS OF ONE HEMISPHERIC STRATOSPHERE

Seasonal adjustment of tropopause level	10%
Mean meridional circulation	43%
Stratospheric exchange between hemispheres	16%
Large-scale eddies (jet streams)	20%*
Small-scale eddies	negligible
TOTAL	89%

---

* An average mass flow of 4 x 10^{17}g per cyclogenetic event (9,10,53) times 31 cyclonic disturbances per year between 40° and 60°N and 70° to 180°W (11) would yield 12.4 x 10^{18}g in that sector per year, or approximately 3.72 x 10^{19}g per year to the whole northern hemisphere in a deliberate overestimate. Mohnen's et al. (26) estimate of an eddy flux of 4 x 10^{20} g/year is an overestimate of at least a factor of five and is in disagreement with other evidence of mass fluxes from the stratosphere.

Whereas there is some uncertainty as to the exact contribution of each of these processes to the total mass exchange across the boundaries of one hemispheric stratosphere, the total flux estimate is in excellent agreement with the observed depletion of Sr^{90} in the northern and southern hemisphere stratospheres after the nuclear test ban treaty went into effect and before the resumption of atmospheric nuclear testing by France and China.

For the northern-hemisphere stratosphere, where Sr^{90} was injected prior to 1963, the depletion of this relatively long-lived radionuclide ($T_{\text{radioactive}} \gg T_{\text{atmospheric residence}}$; T are characteristic e-folding times) can be formulated as follows:

$$\frac{\Delta N}{\Delta t} = -\frac{1}{T} N \qquad \text{(Eq. 1)}$$

T is the e-folding stratospheric residence time, N is taken to be 100%, ΔN is 89% according to the estimates listed above, Δt is 1 year. From these values one arrives at T = 1.12 years or 13.4 months, in agreement with Sr^{90} data (Figure 5). For the southern-hemisphere stratosphere we have to write

$$\frac{\Delta N}{\Delta t} = -\frac{1}{T} N + S \qquad \text{(Eq. 2)}$$

where S = 16% is the "source" consisting of the import from the northern hemisphere, and ΔN = 89% - 16% = 73%. Again assuming N = 100% and Δt = 1 year, we arrive at T = 1.75 years or 21 months, which is in excellent agreement with the data presented in Figure 5.

Unfortunately O_3 is not a passive tracer like Sr^{90} which, once injected into the stratosphere, is subject only to transport processes. There are continuous, but time-variable, photochemical sources and sinks of O_3 acting in both hemispheres. Also the transport processes which remove O_3 from the stratosphere are variable with short-term, seasonal, and long-term fluctuations.

To asses the impact of transport processes across the tropopause on low-tropospheric ozone concentrations we can limit ourselves to O_3 concentrations observed in the vicinity of, or slightly above, the mid-latitude tropopause level, and to the *downward* directed mass fluxes in these latitudes. The upward flux of tropospheric air into the stratosphere, which takes place mainly in low latitudes, can be ignored in our estimates, because it does not contribute positively to the tropospheric ozone burden.

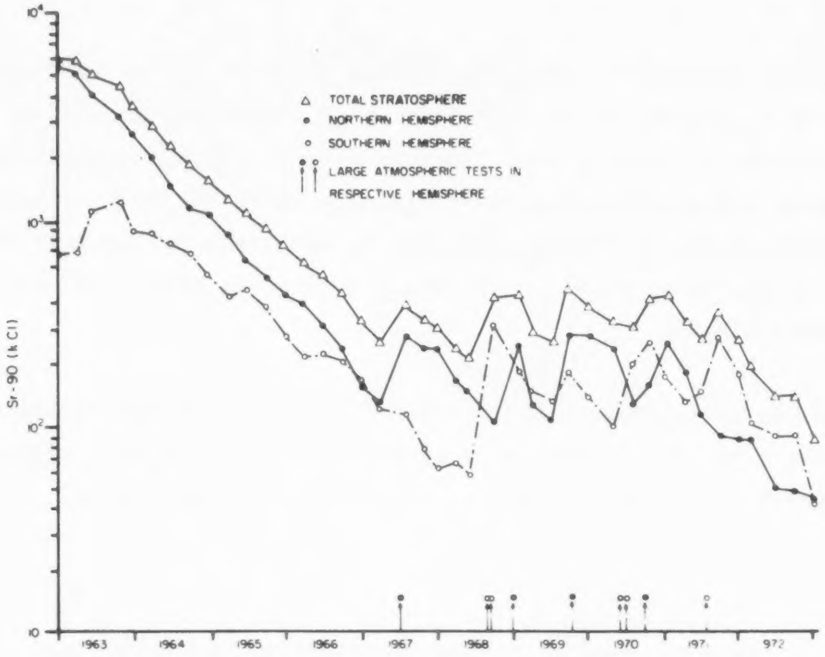


Figure 5. Stratospheric inventory of ^{90}Sr.

Source: Krey, P.W., M. Shonberg, and L. Toonkel. Updating Stratospheric Inventions to January 1973. Report HASL-281. I-130-I-142. U.S. Atomic Energy Commission, Washington, D.C., 1974.

The following evidence can be called upon: cross-sections provided by Dütsch (49) (see reference 33) and reproduced in Figure 6 show average ozone concentrations of 80 nanobars (nb) near the 300-mb level in middle and high latitudes of the northern hemisphere during the cold season. Conversion of these concentration units into ozone mixing ratios, r_3, is accomplished by the relationship

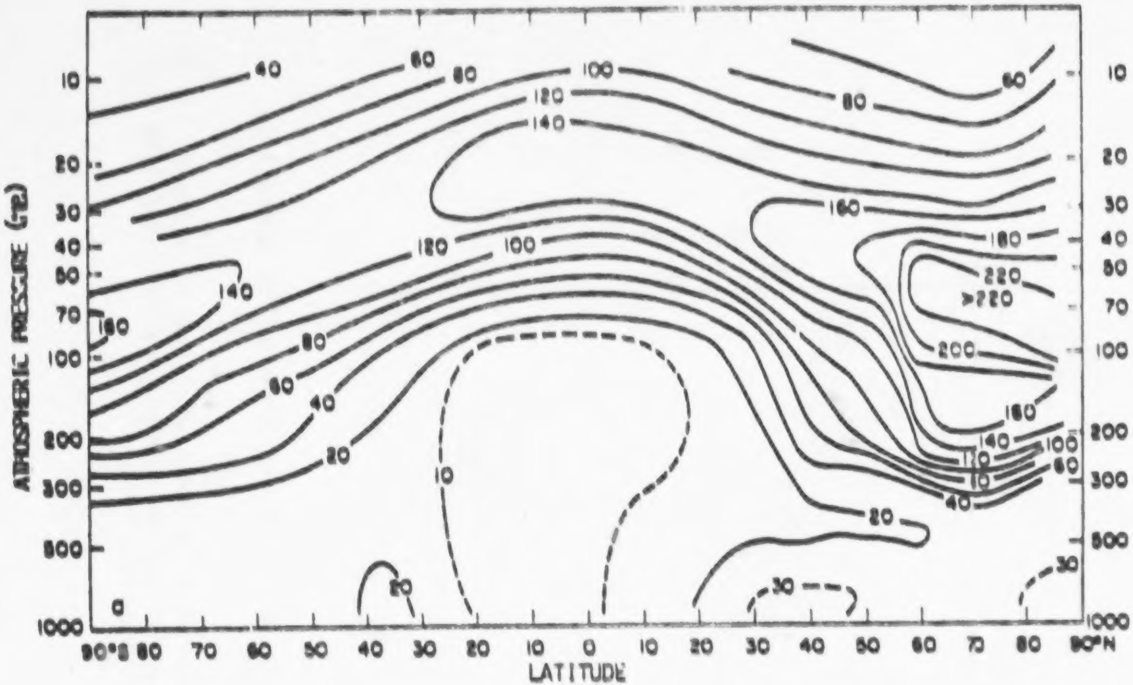
$$r_3(\mu g/g) = \frac{2.871 \times 10^{-3}\ p_3(\text{nanobars})}{1.732 \times 10^{-3}\ p(\text{mb})} \qquad \text{(Eq. 3)}$$

where p is the atmospheric pressure. Hence 80 nb at 300 mb corresponds to 0.44 μg/g of O_3 mixing ratios. Inspection of individual ozonesonde ascents (14,33,36,37,55-57) reveals that 0.5 μg/g sets a convenient *upper* limit of *average* ozone concentrations a short distance above the tropopause. Actually, ozone concentrations at tropopause level in mid-latitudes usually are somewhat lower, as is evident from Figure 7, which depicts an intrusion case of stratospheric ozone (58).

In the following table (50) we have listed mass fluxes across the tropopause during different seasons as computed by J.F. Louis (see reference 33), and pertaining to the mean-meridional circulation contribution.

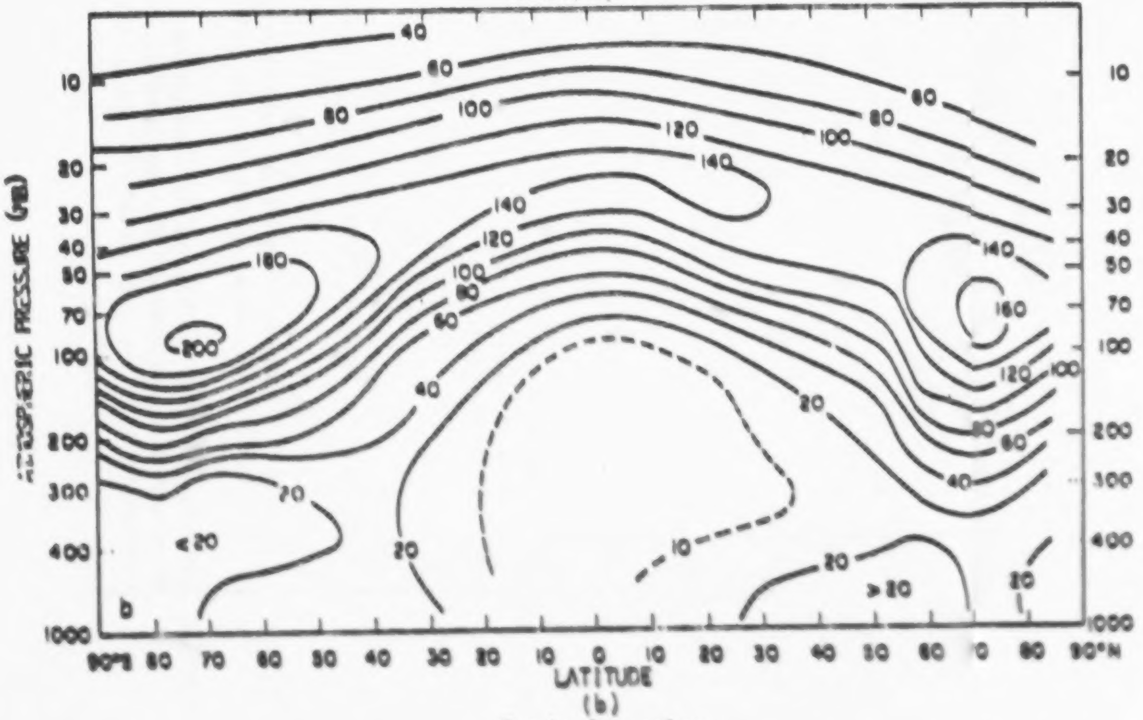
TABLE 2. MASS FLUX FROM STRATOSPHERE TO TROPOSPHERE ACCOMPLISHED BY HADLEY CELL CIRCULATION

Season	Mass Flow (units 10^{12} g/sec)	Total Flux in Three Months (10^{17} g)	Contribution in Northern Hemisphere (10^{17} g)
Dec. - Feb.	10	788	622
March - May	4	311	272
June - Aug.	7.5	583	389
Sept. - Nov.	7	544	560
Annual flux, northern hemisphere			1843×10^{17} g



(a)

March/April



(b)

October/November

Figure 6. Pole-to-pole cross-section of vertical ozone distributin in nb (1 nb = 0.1 N/m^2).

Source: Dütsch, H.U. Photochemistry of Atmospheric Ozone. Advance in Geophysics, 15:219-322, 1971.

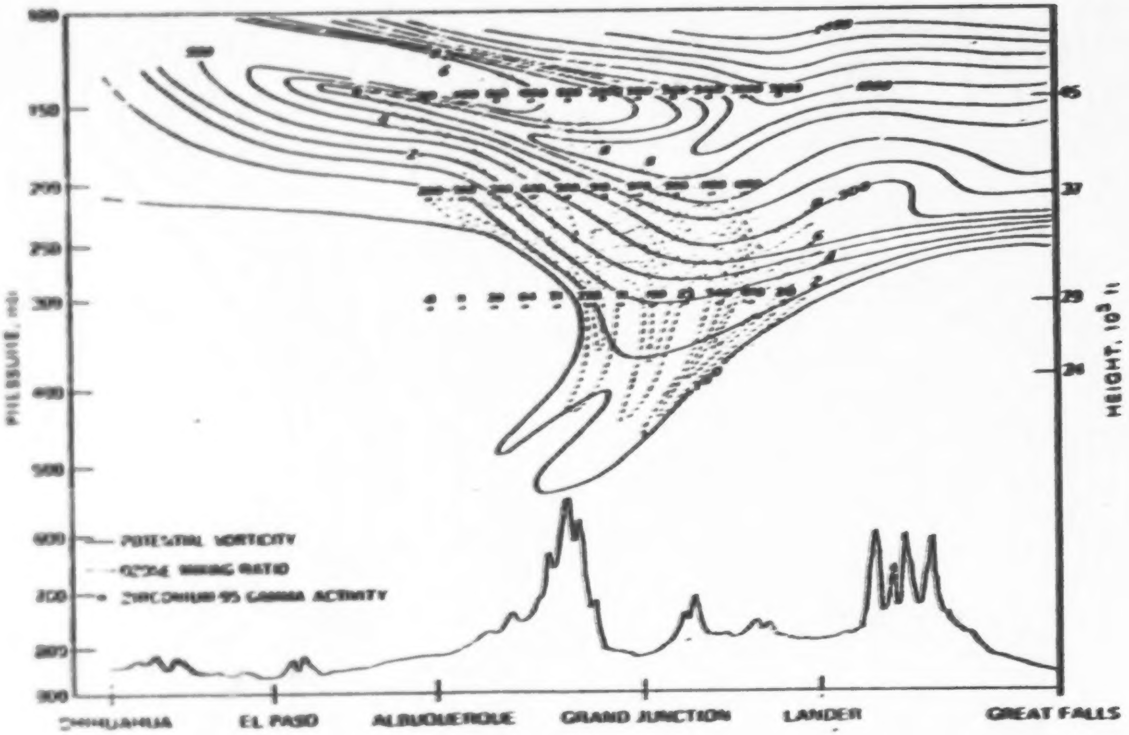
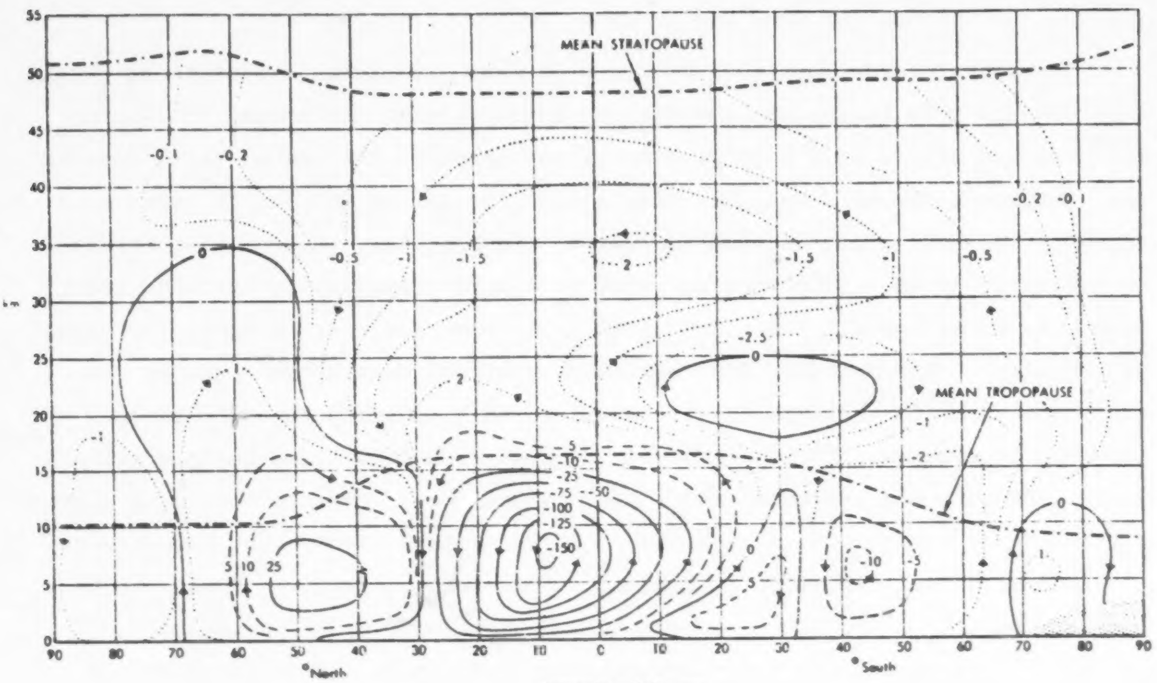


Figure 7. Vertical cross-section of potential vorticity (10^{-10} cm sec deg/g), ^{95}Zr activities (dpm/scf), and ozone mixing ratios (10^{-7} g/g).

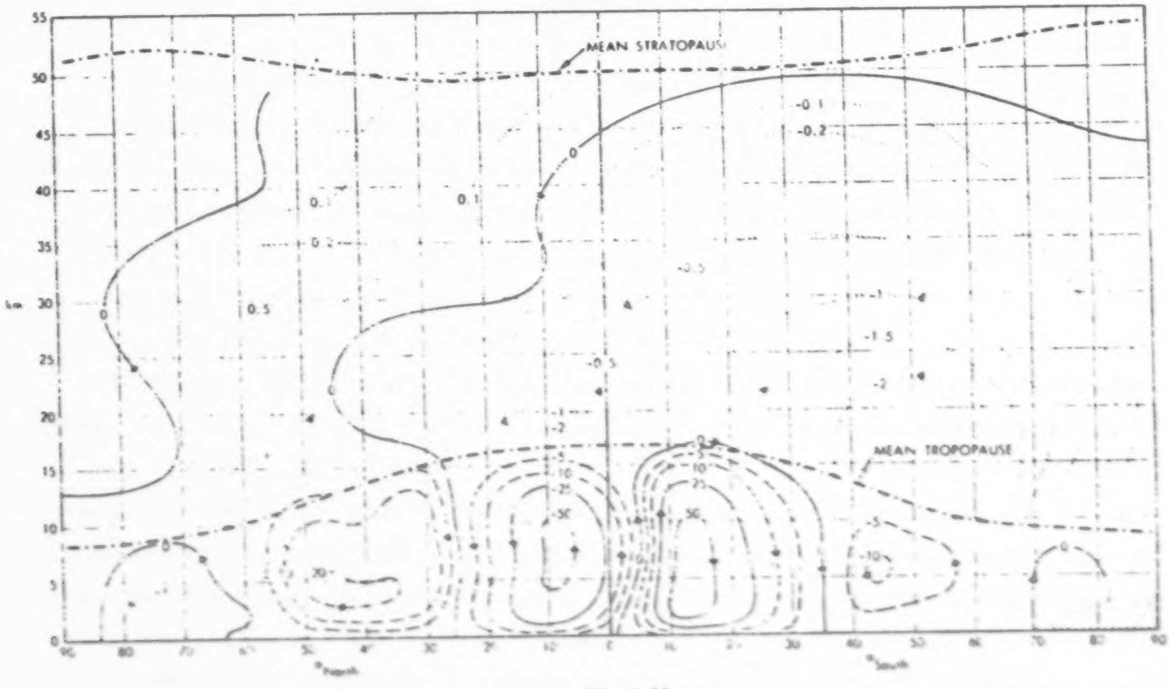
Source: Danielsen, E.F., R. Bleck, J. Shedlovsky, A. Wartburg, P. Haagenson, and W. Pollock. Observed Distribution of Radioactivity, Ozone and Potential Vorticity Associated with Tropopause Folding. J. Geophys. Res., 75(12):2353-2361, 1970.

Strongest cross-tropopause fluxes by a mean meridional circulation, according to this table, are encountered during winter and amount to 10×10^{12}g/sec of air or to 5×10^{6}g of ozone per second. The annual total flux in the northern hemisphere would be 1843×10^{17}g of air or 9.215×10^{7} tons of ozone by the action of the mean meridional circulation. This value compares to estimates of 40×10^{7}g tons per year on a hemispheric basis by Junge (20), (see also Mohnen et al. (26)) and of 65×10^{7} tons per year by Aldaz (30) (see Reiter (37)). Pruchniewicz (59) estimates a global destruction rate at the surface of 75×10^{7} tons per year, 3/4 of which is thought to occur in the northern hemisphere. His estimate was derived from world-wide surface measurements, aircraft measurements, and balloon soundings. Obviously there is quite a discrepancy between these estimates. Aldaz' values involve the measurement of vertical ozone concentration gradients over land and water. However, the ozone concentrations near the ground used by Aldaz and by Pruchniewicz most likely were contaminated by tropospheric sources, hence the computed fluxes should not be ascribed entirely to stratospheric sources.

We will have to take into account that the major downward transport during most of the year, accomplished by the mean meridional circulation, occurs in middle latitudes and not over the entire hemisphere (Figure 8a,b,c,d). A flux of 6×10^{6}g/sec of ozone during the period December-February through the tropopause of middle latitudes can be translated into a flux of 0.4×10^{-7} g/m^{2}sec, if this downward transport by the mean meridional circulation is confined to only one-half of the area of the northern hemisphere. This number compares to a flux of 0.5×10^{-7}g/m^{2}sec estimated by Junge (20) (see Reiter, (37)) as an annual average value. An annual flux of ozone of 9.215×10^{7} tons translates into a flux of 0.23×10^{-7}g/m^{2}sec, if concentrated over half the area of one hemisphere. This number does not yet include the effects of eddy transport processes in the jet-stream region, which also have a preponderance in middle latitudes and, on the average, might increase the above estimate by 50%. Such an increase, however, still leaves us short of the estimates by Junge and Aldaz, probably because of anthropogenic contamination of some of their data.



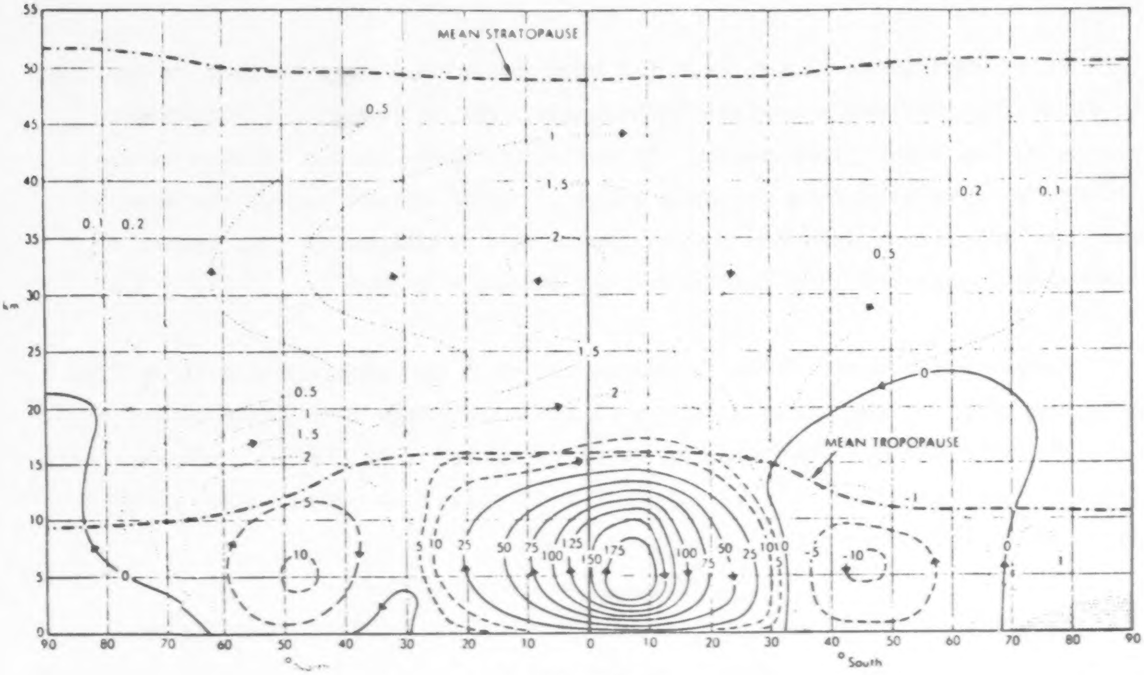
December–February.



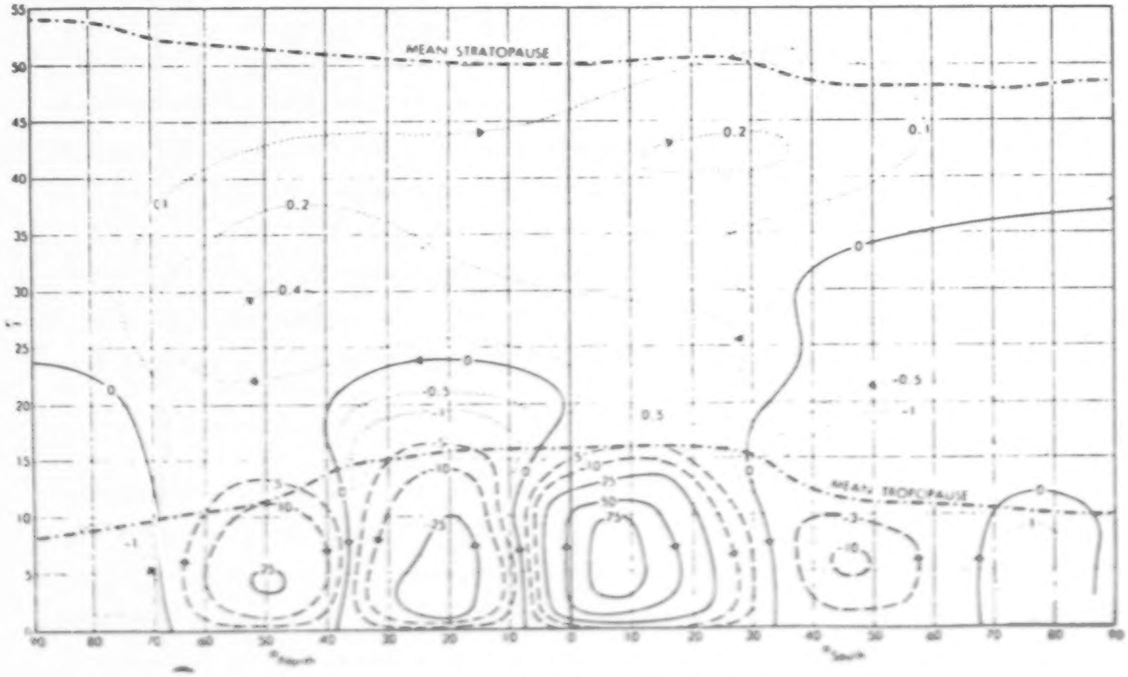
March–May

Figure 8. Mean meridional circulation (mass flow in units of 10^{12} g s^{-1}) for the four seasons [from Louis].

Source: Reiter, R., H.J. Kanter, R. Sladkovic, and K. Potzl. Measurement of Airborne Radioactivity and Its Meteorological Application. Part V. Annual Report 1 April 1973 - 31 July 1974. Institut Fur Atmospharische Umweltforshung. ERDA Document No. NYO-3425-12. 1976.



June–August.



September–November.

Figure 8. (Continued)

It is logical to assume that the mean meridional circulation, as depicted in Figure 8, provides a certain background level of ozone of stratospheric origin in the lower troposphere. To arrive at these concentrations we can divide the flux estimates provided above in units of g/m^2sec by the mean vertical velocities in m/sec prevailing in the troposphere. The result of such computations will be concentrations of ozone in g/m^3.

Junge (see Reiter, (37)) estimates the mean tropospheric residence time of ozone to be of the order of 3.3 months. An average tropopause height of 12 km thus would yield a mean transit velocity of 1.4×10^{-3} m/sec. Together with Junge's flux value of $0.5 \times 10^{-7} g/m^2sec$ this yields a concentration of 35.6 $\mu g/m^3$ or approximately 16.8 nanobars of ozone.

On the other hand, we can estimate vertical velocities from the mass fluxes shown in Figure 8, using the expression

$$\bar{w} = \frac{1}{2\pi R^2 \rho \cos \phi} \frac{\partial \psi}{\partial \psi} \qquad \text{(Eq. 4)}$$

where ψ is the mass-weighted stream function depicted in Figure 8 in units of 10^{12} g/sec, R is the earth's radius, ρ is air density, and $\partial \phi$ is the latitude difference in radians. Using the December-February data between 10°N and 40°N and at a height of approximately 8 km, one arrives at $\bar{w} = 2.74 \times 10^{-3}$ m/sec. Together with a flux of $0.4 \times 10^{-7} g/m^2sec$ estimated earlier this vertical velocity will result in a mean background concentration of O_3 of 14.6 $\mu g/m^3$, less than half of what Junge's data would yield. For comparison, the present Federal standards, specifying maximum concentrations not to be exceeded for longer than 1 hour, are 160 $\mu mg/m^3$.

From a comparison of these values we can estimate that the natural *mean* background of O_3 of stratospheric origin in the mid-latitude troposphere produced by the mean meridional circulation should be of the order of 10 to 20 percent of the Federal 1-hour standard. Actually, the lower one of these two percent values appears to be more appropriate as a conservative estimate of mean background concentrations, because the assumption of an ozone mixing ratio of 0.5 $\mu g/g$ at tropopause level, which entered into the above estimates, is a conservative overestimation. Sticksel (39) on the other hand obtains a "tropospheric background" of approximately 80 percent of the 1-hour Federal standard from the ozonesonde observations of the 1960's. These data are, however, suspect of anthropogenic contamination (Reiter, (60)), and do not consider further dilution within the planetary boundary layer.

Using a different approach, Reiter (7) estimated the mean background of stratospheric O_3 in the troposphere to be approximately 5 percent of the Federal standard 1-hour maximum concentration. This number was arrived at by estimated Sr^{90}/O_3 ratios in the lower stratosphere and, using these ratios as a conservative quantity, inferring the ground-level ozone concentrations from radioactive fallout measurements as compiled by the U.S. Public Health Service Radiation Surveillance Network. As will be pointed out later, this value of 5% may have been an underestimate.

We have to expect some interannual variability of the mean meridional circulation and its effects on background levels of O_3 in the troposphere. Only a few studies exist that point out that the interannual variability of the atmospheric general circulation is significant, without testing the specifics of transport processes (61-65). Mean meridional circulation patterns in the stratosphere published by Vincent (66) indicate stronger downward fluxes in the lower stratosphere of middle latitudes during January, March, and May 1965 than during the same months of 1964. This is in agreement with the observations in Figure 1, suggesting that the variability in the various transport mechanisms may have as much to do with ozone variability as the sunspot cycle. (A number of literature references explore the possibility of correlations between atmospheric circulation patterns and the sunspot cycle.)

Our mass-budget of stratospheric-tropospheric interchange ascribes approximately 20% of the equivalent of one hemispheric stratosphere to enter the troposphere within 1 year through large-scale eddy mixing, mainly in the jet-stream region. Even though this effect is less than one-half of that of the mean meridional circulation, it will influence low-tropospheric ozone concentrations more profoundly. Whereas vertical velocities ascribed to the mean meridional circulation are typically of the order of a few millimeters per second, subsidence associated with synoptic-scale jet-stream systems is of the order of a few cm/sec (see for example, reference 53). Such velocities would entail a transit time of stratospheric air intrusions through the depth of the troposphere of a few days (order of magnitude 3 to 5 days, on the average). Less mixing will occur with these shorter transit times than with the slow-acting mean meridional circulation. Quantitative estimates of these mixing processes will be made in the subsequent section.

It has been demonstrated in numerous studies (see, for example, references 9,10,43,53,67-70) that stratospheric air intrusions into the troposphere on a massive scale occur only through the "tropopause break," i.e., a discontinuity in the tropopause level observed on the anticylonic side of the jet-stream systems of subtropical and middle latitudes. Especially the polar-front jet stream with its associated frontal system offers a convenient "sliding surface" along which stratospheric air masses can move into the lower troposphere without excessive mixing and in a matter of a few days. For the lack of a frontal system the "subtropical jet stream" offers less opportunity for a rapid air mass transit through the depth of the troposphere. Therefore, this jet-stream system is of only secondary concern when studying the effects of stratospheric air intrusions on high ozone concentration levels near the ground. The subtropical jet, however, still is important in maintaining the "natural background" of ozone of stratospheric origin observed in the troposphere and discussed earlier. Wide-spread subsidence motion underneath the subtropical jet-stream belt of winter actually contributes to the mean meridional motion effects described before.

The vertical turnover and mixing of the atmosphere is more violent in the polar-front jet-stream region than in the subtropics. Stratospheric air-mass intrusions into the troposphere coincide with a tropopause-folding process (8). The stratospheric air masses start their descent in the rear left quadrant of a jet maximum (Figure 9) in the course of the development of a cyclonic disturbance of the westerly flow (68,71). Mahlman (11) has shown that the magnitude, or amplitude of such a disturbance — expressed in terms of a cyclone index that measures the meridionality of wind directions in mid-latitudes and in the upper troposphere — is positively correlated with the amount of stratospheric air extruding into the troposphere and/or with the rapidity with which it traverses the depth of the troposphere.

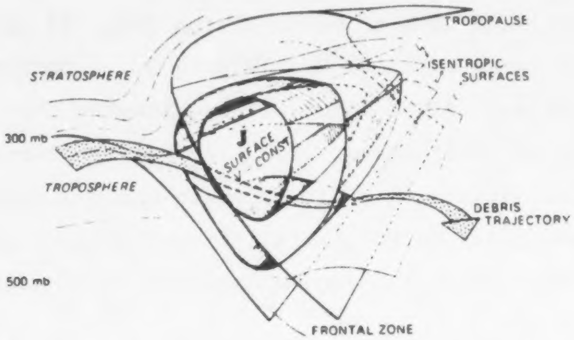


Figure 9. Schematic three-dimensional view of mass flow from stratosphere to troposphere near a jet stream. Isentropic surfaces are indicated by thin lines. Surfaces of constant wind speed, boundaries of the frontal zone, and the tropopause are marked by heavy lines.

Source: Reiter, E.R. A Case Study of Radioactive Fallout. J. Appl. Meteorol., 2(6):691-705, 1963.

Unfortunately, at this time we have only a very poor statistical grasp of the effects of the intensity of cyclonic disturbances on the amount of stratospheric air injected into the troposphere. Our only estimates refer to a few case studies which were of strong enough intensity to produce such fallout (9,10,53) and one which did not (70). The intrusions which produced radioactive fallout were massive and quick enough to reach the lower troposphere in a relatively undiluted state and contained approximately 0.4 to 0.6 x 10^{12} metric tons of stratospheric air. The intrusion studied by Reiter and Mahlman, which did not reach the ground, hence contributed only to the general and diluted radioactivity and ozone burden of the troposphere involved only about 0.25 x 10^{12} metric tons of air. There probably is a cut-off value, not only in terms of Mahlman's cyclone index, but also in terms of tonnage of stratospheric air intrusions which must be exceeded before relatively undiluted stratospheric air comes to rest within a subsidence inversion capping the planetary boundary layer or mixing layer above the earth's surface. We do not know precisely where these cut-off values lie, but we could guess that they are near 2.4 for the cyclone index (for its definition, see reference 71) and near 0.4 x 10^{12} tons for the mass of air involved in the intrusion.

Mahlman (11) counted 31 cyclonic disturbances over the North American sector (70°W to 180°N, and 40°N to 60°N) during 1963, 23 of which met or exceeded the cyclone index value of 2.4 (Figure 10). During 1964, again, 31 disturbances were counted, 23 of which met or exceeded the "critical" value, suggesting little or no interannual variability of the large-scale eddy transport processes in the jet-stream region between these 2 years. The same conclusion can be reached from McGuirk's (72) analysis of eddy available potential (A_E) and kinetic (K_E) energies computed on a hemispheric basis.

Mahlman's analysis (Figure 10) shows little, if any, seasonal variability of the number of cyclonic disturbances passing the North American sector, nor does it reveal a significant seasonal march of the intensity of these episodes. McGuirk (72) showed from a 10-year data base that the mean seasonal double-amplitude (the difference between maximum and minimum values) for A_E is about 65% of the mean value (Figure 11). It is approximately the same for K_E. Maxima in both parameters occur in January, suggesting, on the average, a tendency of stronger stratospheric air intrusions during winter than during summer. According to Figure 4, highest stratospheric ozone concentrations in the (lower) stratosphere occur in April. Because of the vertical velocities characteristic of the mean meridional circulation, one should expect a delay by 1 month of the appearance of the ozone maximum of stratospheric origin at the ground, moving it into May (see also, reference 73). The jet-stream transport effects, superimposed upon the mean background and modulating it with the passage of cyclonic and anticylonic disturbances, should yield — on the average — maximum stratospheric ozone effects near the ground in mid-latitudes during March and April. As we can see from Figure 10, the radioactive fallout distribution over the United States, and presumably also the O_3 ground-level concentrations due to stratospheric import, peak in April-May. The *average* mass transport from the stratosphere to the lower troposphere in mid-latitudes, therefore, is more strongly influenced by the seasonal variability of the stratospheric reservoir of radioactivity or ozone, hence by the

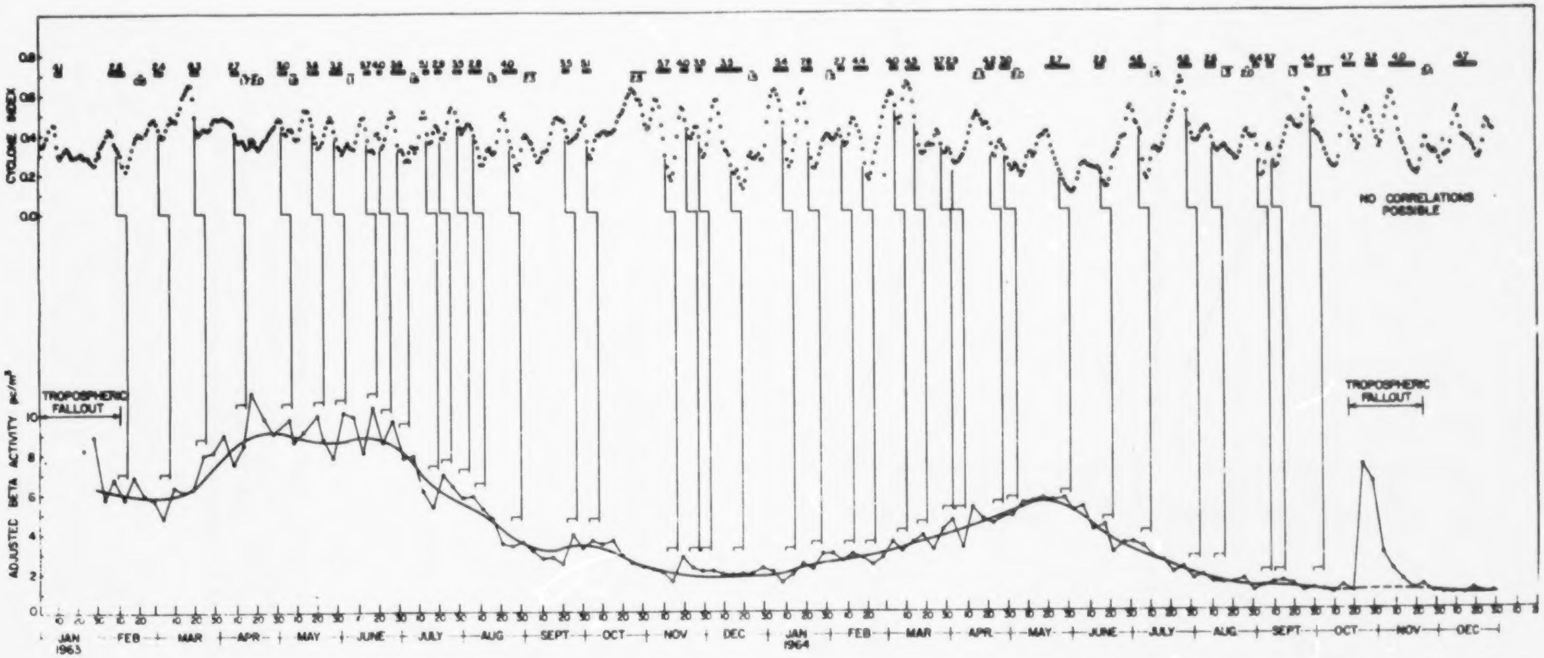


Figure 10. Time series of comparison between cyclone index, C, and shorter period fallout fluctuations. Upper part of diagram is smoothed cyclone index series. In the lower part: thin connected lines are 5-day mean age-adjusted gross beta activity; heavy smooth line gives mean monthly fallout values. Vertical lines from cyclone index show the high percentage of fallout increases within 5 days after rapid cyclone index decreases. Numbers across top of figure are values of 100 $(C_1 - C_2)/\Delta t$ computed during each cyclone index decrease. Numbers above heavy bars are greater than critical value of 2.5 and numbers below thin bars are below 2.5.

Source: Mahlman, J.D. Relation of Tropopause-Level Index Changes to Radioactive Fallout Fluctuations. Atmospheric Science Technical Paper No. 70. Colorado State University, Fort Collins, Colo., 1963. pp. 84-109.

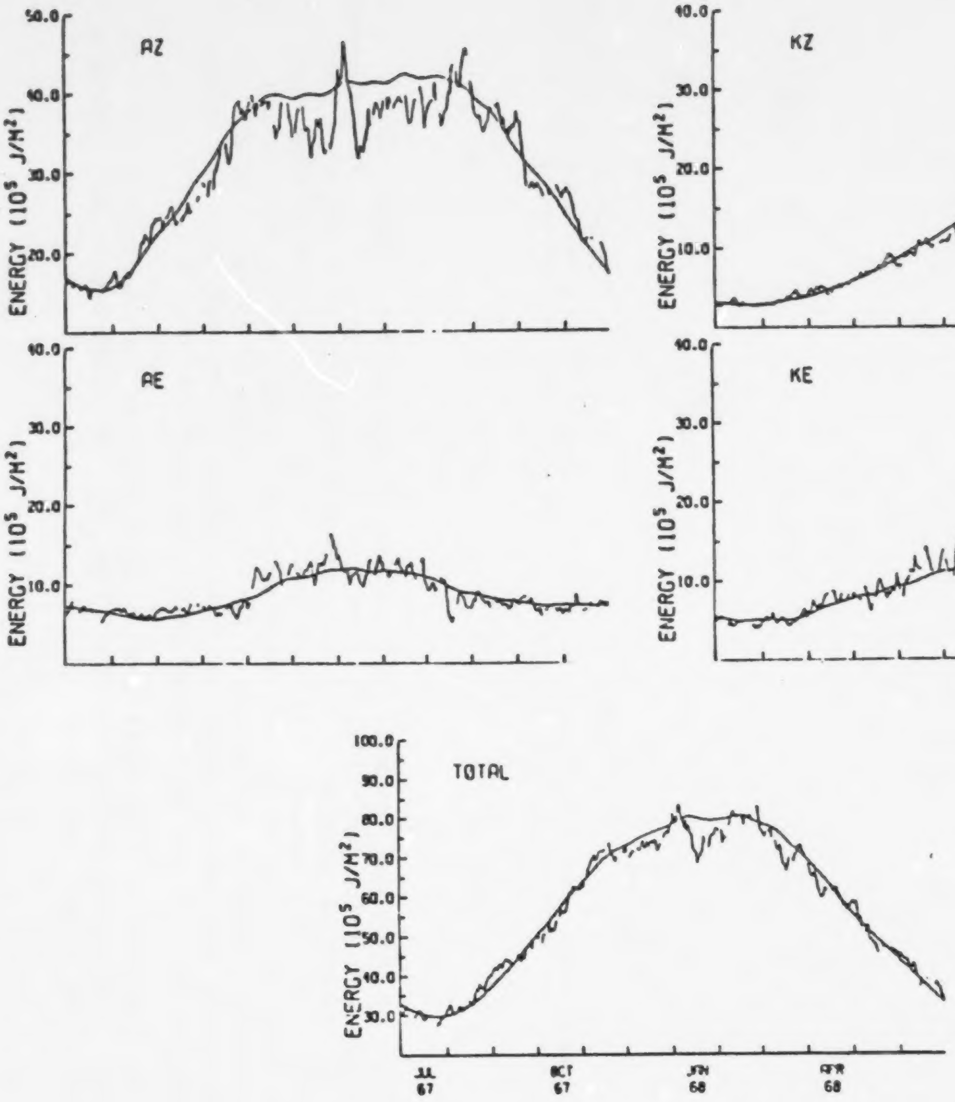


Figure 11. Daily values of energy by mode and for the total of available potential plus kinetic energy from July 1967 through June 1968. The smoothed line represents the annual energy obtained from averaging nine individually smoothed annual energy series.

Source: McQuirk, J.P. Fluctuations in the Atmosphere's Energy Cycle. Environmental Research Paper No. 6, Colorado State University, Fort Collins, Colo., 1977.

mean meridional circulation in the stratosphere, than by the seasonal behavior of jet-stream and cyclogenetic activities. This statement is corroborated by Table 1.

Future investigations will have to establish a correlation between the intensities of cyclonic disturbances in mid-latitudes and the amount of stratospheric air transferred into the troposphere by these disturbances. Also a better frequency count of these disturbances around the whole hemisphere would be quite useful.

The impact of large-scale eddy motions in the jet-stream region of mid-latitudes on surface ozone concentrations has been estimated by Reiter (50,74). Average O_3 concentrations in the lower stratosphere as established by Dütsch (49) for the appropriate season were compared to Sr^{90} distributions measured by aircraft or balloon (75). An example for 1963 is shown in Figure 12. Corrections were made for the depletion of radioactivity from the stratosphere and for seasonal O_3 variability to bring different observational periods into agreement with each other (Figure 13).

Surface radioactivity measurements (reported as total activity in pCi/m^3) were available from the U.S. Public Health Service Radiation Surveillance Network. The assumption was made that the Sr^{90}/O_3 concentration ratios inferred for the lower stratosphere would remain constant during rapidly proceeding stratospheric air intrusions into the lower troposphere. Sr^{90} and O_3 of stratospheric origin would be subject to the same transport and mixing processes. Hence, if the Sr^{90} fallout concentration levels at the ground were known, the stratospheric contribution to concentrations of O_3 associated with the same air mass could be derived.

Since surface radioactivity was given in terms of total activity, estimates had to be made of the specific Sr^{90} contribution towards this total activity. Assuming that during spring of 1963 the bulk of the radioactive debris in the stratosphere was less than 1 year old, Reiter (74) derived a contribution of Sr^{90} towards total radioactivity of 1 percent from fission yield and radioactive decay curves. Table 3 (11) shows that such a percent

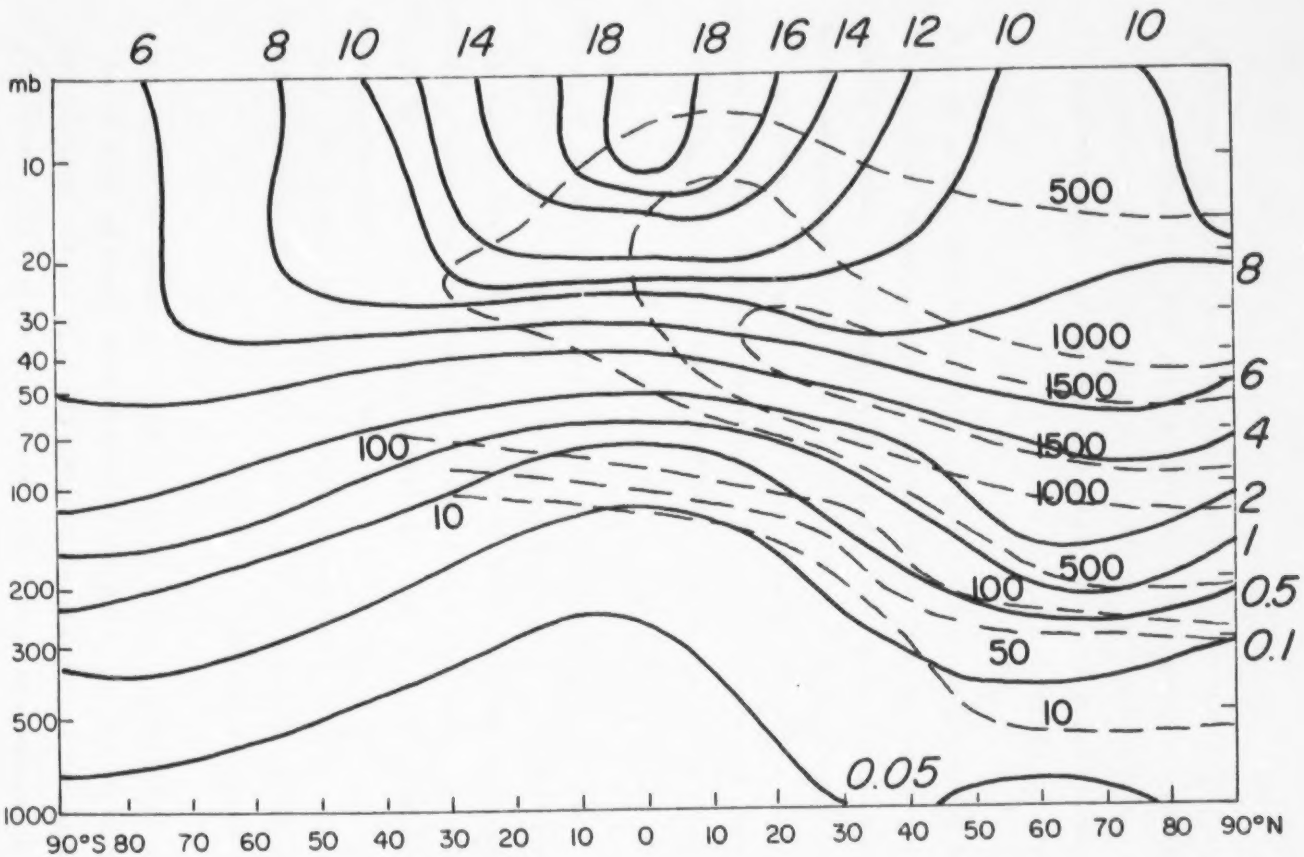


Figure 12. Mean ozone distribution for March-April (solid lines, slanting numbers, μg/g) and Sr^{90} distribution for May-August 1963 (dashed lines, vertical numbers, dpm/1000 SCF).

Source: Reiter, E.R. The Transport of Radioactive Debris and Ozone from the Stratosphere to the Ground. Report to Stanford Research Institute, Nov. 22, 1975. 36 pp.

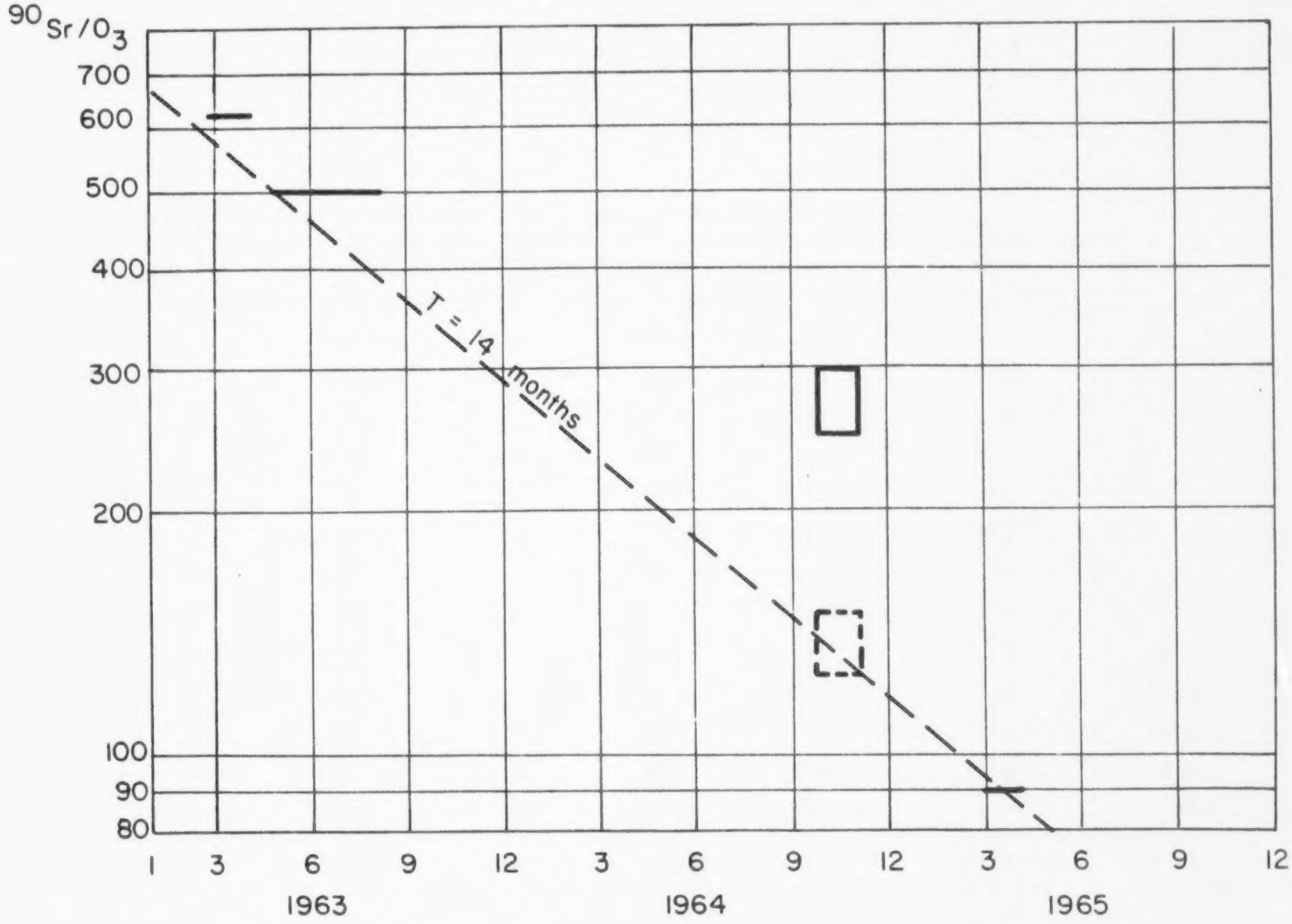


Figure 13. $^{90}Sr/O_3$ ratios as a function of time (see text for explanation).

Source: Reiter, E.R. The Transport of Radioactive Debris and Ozone from the Stratosphere to the Ground. Report to Stanford Research Institute. Nov. 22. 1975. 36 pp.

TABLE 3. PERCENTAGE CONTRIBUTION OF PARTICULAR NUCLIDES IN TOTAL MONTHLY RADIOACTIVE DEBRIS MEASURED IN RAINFALL AT WESTWOOD, NEW JERSEY. HALF-LIFE OF EACH NUCLIDE IN DAYS IS GIVEN IN PARENTHESES.

	PERCENTAGE CONTRIBUTION OF NUCLIDE					
	Sr - 90 (10,120d)	Sr - 89 (50.5d)	Ce - 144 (285d)	Zr - 95 (65.0d)	Cs - 137 (11,140d)	Ce - 141 (33.1d)
January 1963	0.9%	26.2%	21.5%	44.8%	1.4%	5.1%
February	1.2	23.8	34.2	34.2	1.6	5.0
March	1.6	18.0	36.8	30.8	2.3	10.7
April	2.0	15.2	49.7	25.8	2.8	4.4
May	2.2	11.4	44.7	28.2	3.2	10.2
June	2.8	10.1	51.6	26.2	4.1	5.0
July	4.0	9.6	55.6	25.6	5.2	
August	3.0	5.5	65.2	20.0	6.4	
September	3.9	4.9	69.4	15.4	6.4	
October	3.9	3.9	72.6	13.2	6.4	
November	3.5	2.1	75.3	12.3	6.8	
December	3.8	1.3	78.8	11.8	4.3	
January 1964	3.8	0.9	80.9	7.1	7.3	

Source: Mahlman, J.D. Relation of Tropopause-Level Index Changes to Radioactive Fallout Fluctuations. Atmospheric Science Technical Paper No. 70. Colorado State University, Fort Collins, Colo., 1963. pp. 84-109.

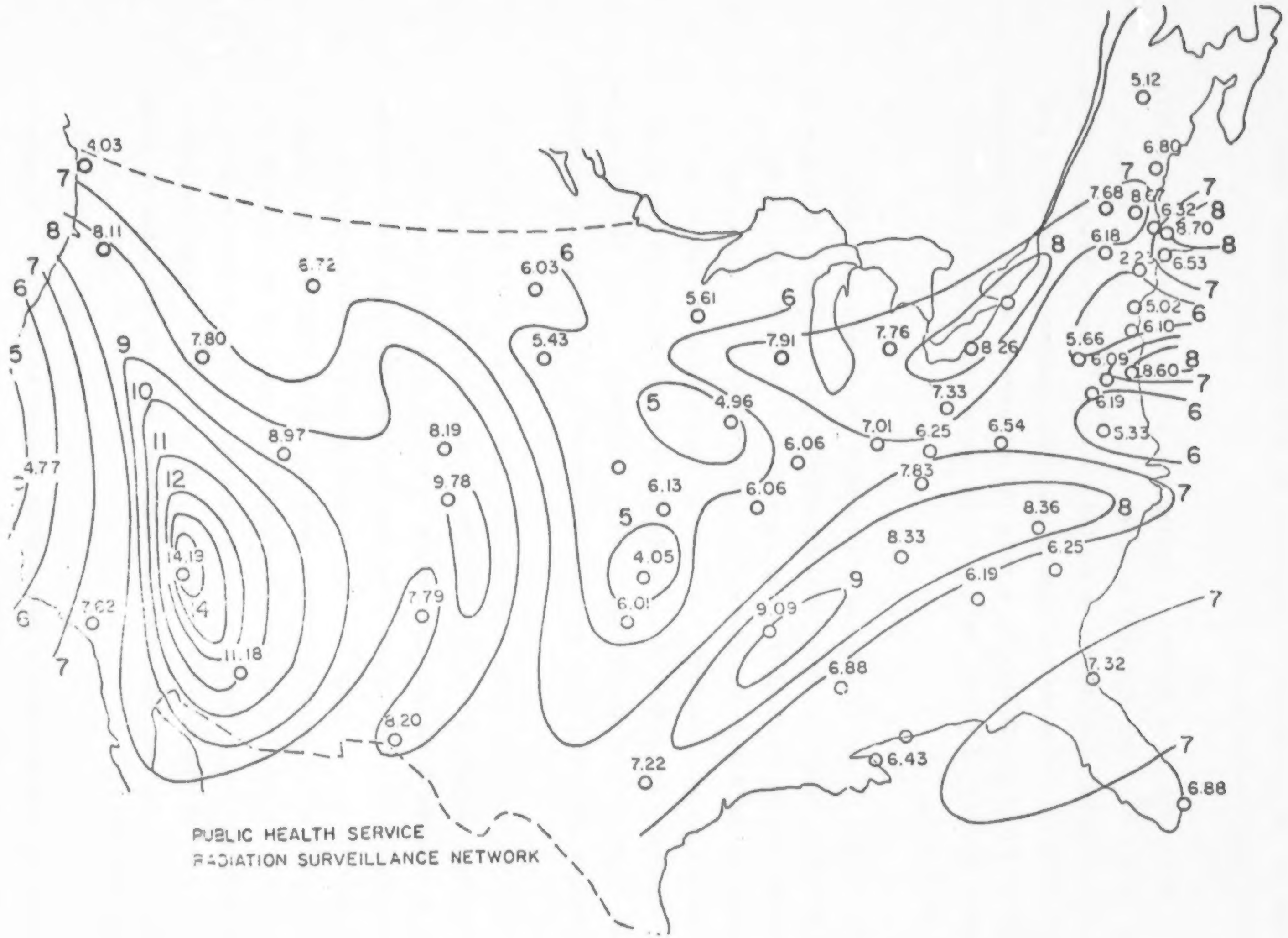
value would, indeed, have been correct for January and February 1963. For the first half year of 1963, however, a contribution of 2 percent by Sr^{90} would have been a more appropriate assumption.

Figure 14 shows the mean fallout distribution for the period January-July 1963 in units of pCi/m^3. For the period March-April 1963 the lower-stratospheric Sr^{90}/O_3 ratio was determined to be 620, with Sr^{90} concentrations given in dpm/1000 SCF (disintegrations per minute per 1000 standard cubic foot) and O_3 concentrations in µg/g. Assigning a value of 2 percent to the contribution of Sr^{90} to total fallout, 1 pCi/m^3 in Figure 14 would correspond to approximately 0.002 µg/g of O_3.

Disregarding the local fallout pattern around the Nevada test site, maximum *mean* fallout (measured over sampling periods of 24 hours) in Figure 14 of 9 pCi/m^3 corresponded to roughly 0.018 µg/g of O_3. By comparison, the Federal standard 1-hour maximum concentration is 0.1238 µg/g. Thus, the distribution in Figure 14 indicates that the background concentration of stratospheric O_3 near the ground in the mid-latitude jet-stream region might rise to around 15 percent of the Federal 1-hour standard. This value is close to the one ascribed earlier to the effects of the mean meridional circulation.

Figure 15 shows that over the southeastern and eastern United States, but also along the Rocky Mountain Front Range, there is a significant number of days per year during which background levels of O_3 of stratospheric ozone measure higher than 0.02 µg/g. Again, we have to disregard the local effects of the Nevada test site. Maximum 24-hour concentrations of radioactivity observed during 1963 would suggest ground-level O_3 concentrations (averaged over 24 hours) of 0.05 µg/g or slightly less than one-half of the Federal 1-hour standard (Figure 16). Similar maximum 24-hour O_3 concentrations of stratospheric origin at the earth's surface could be inferred from the 1964 maximum fallout distribution, allowing for a higher Sr^{90} contribution to total fallout during that year.

Mean 24-hour O_3 concentrations measured at Zugspitze Mountain, Germany (3000 m above MSL), are shown in Figure 17 (51). The mode value of observa-


PUBLIC HEALTH SERVICE
RADIATION SURVEILLANCE NETWORK
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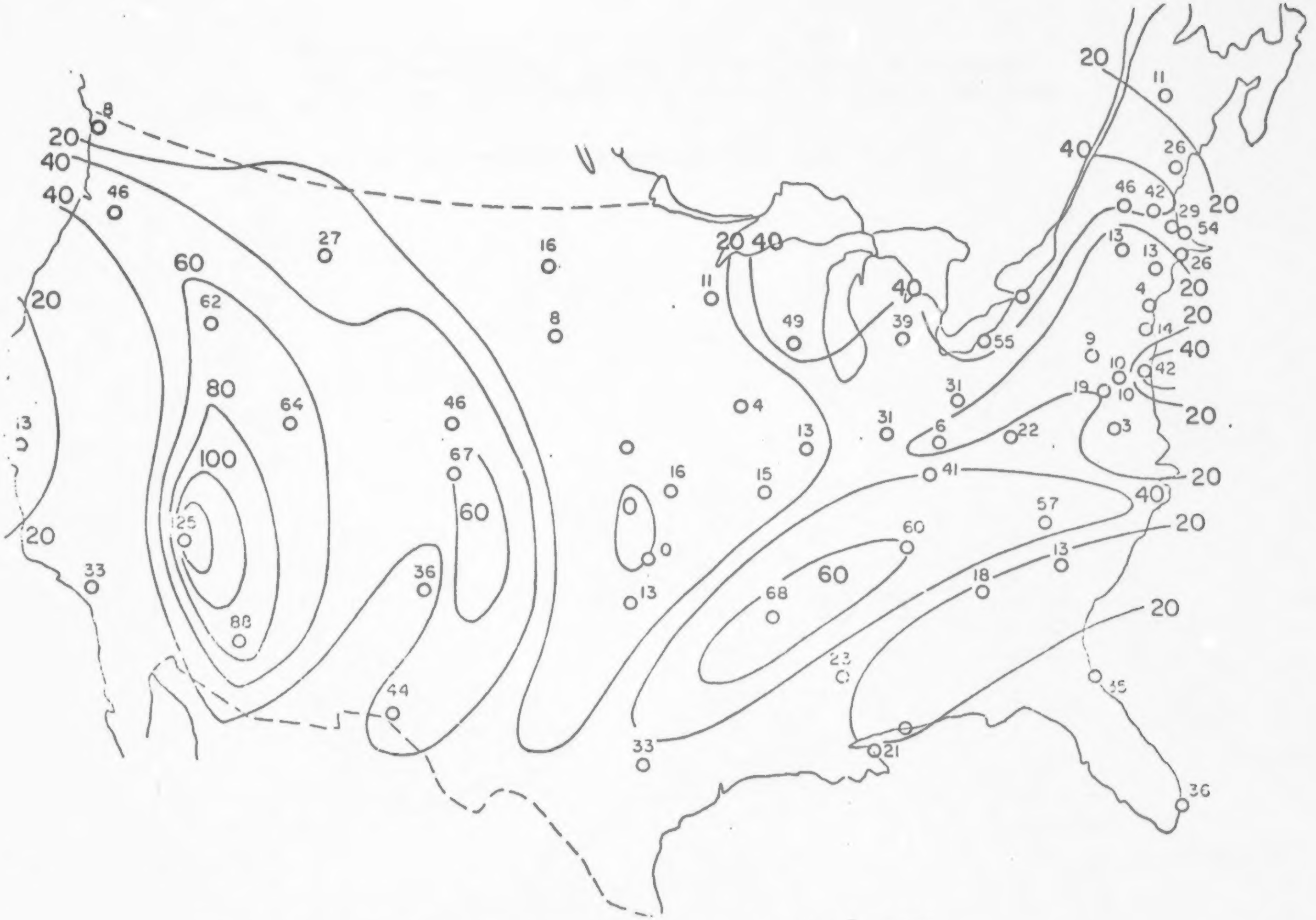
14

Figure 14. Mean Fallout, January-June 1963, pCi/m^3.

Source: Reiter, E.R. The Transport of Radioactive Debris and Ozone from the Stratosphere to the Ground. Report to Stanford Research Institute, Nov. 22, 1975. 36 pp.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9
10
42
40
19
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3
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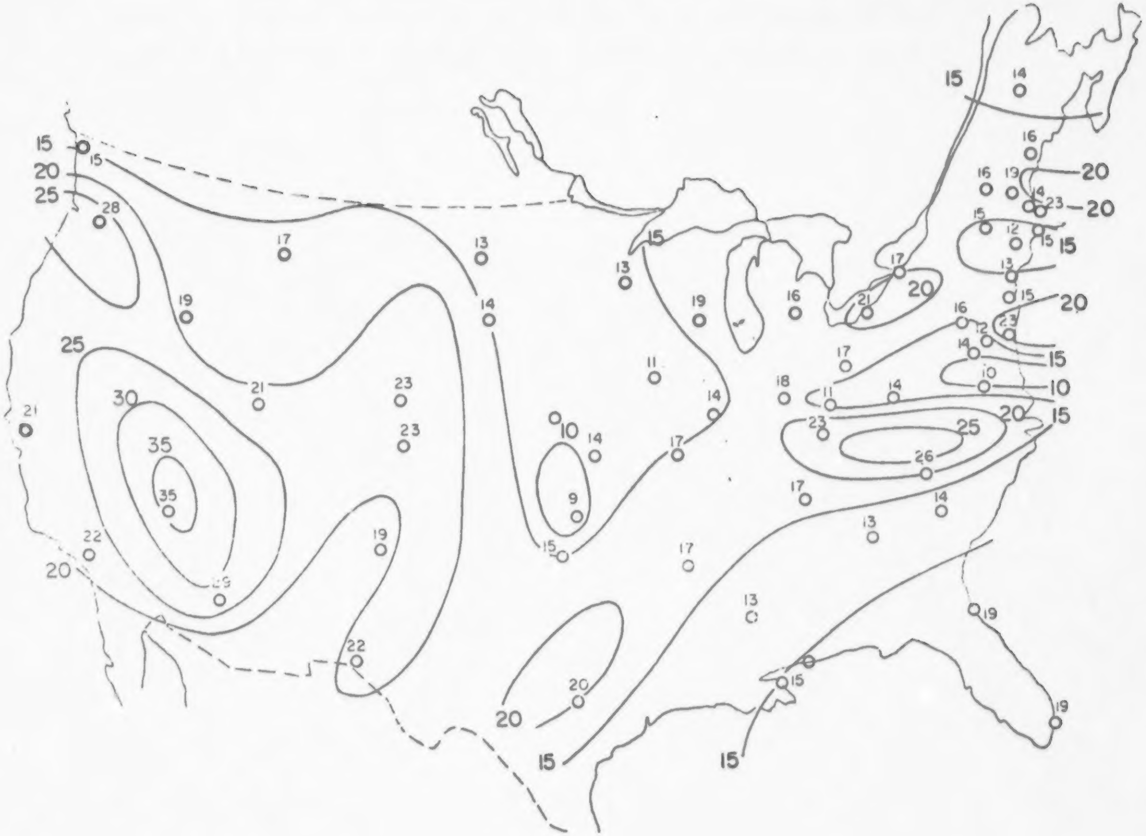
20
35
36

Figure 15. Number of days with fallout ≥ 10 pCi/m^3, 1963.

Source: Reiter, E.R. The Transport of Radioactive Debris and Ozone from the Stratosphere to the Ground. Report to Stanford Research Institute, Nov. 22, 1975. 36 pp.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10
15

Figure 16. Maximum 24-hour fallout 1963, pCi/m^3.

Source: Reiter, E.R. The Transport of Radioactive Debris and Ozone from the Stratosphere to the Ground. Report to Stanford Research Institute, Nov. 22, 1975. 36 pp.

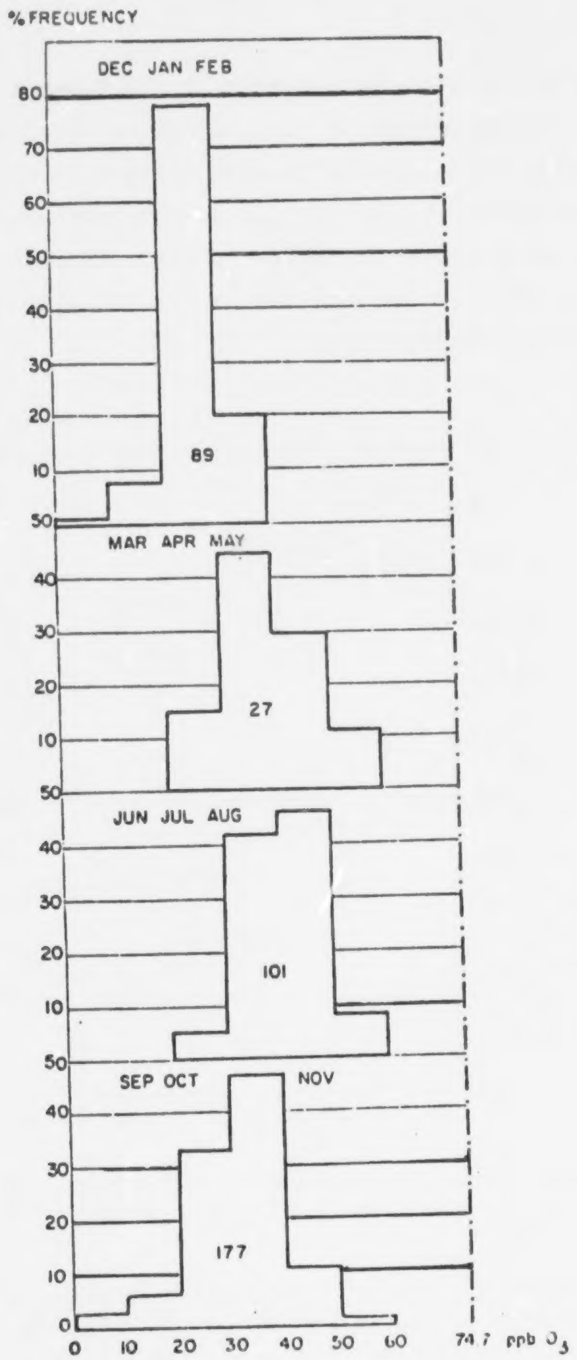


Figure 17. Percent frequency distribution of ozone concentrations (ppb) observed at Zugspitze, Germany, from August 1973 to October 1975. Number of observations is indicated in each histogram.

Source: Reiter, E.R. On the correlation between cosmogenic Be-7 and ozone. Report to Stanford Research Institute, 23 December 1975.

tions appears to lie close to one-half of the Federal 1-hour standard value (indicated by the dashed-dotted line in Figure 17). Allowing for additional dilution between 3000 m and the general terrain level of the eastern United States, the estimates of 0.05 μg/g of 24-hour averaged maximum ozone concentrations made above appear to be reasonable. Aircraft measurements below the tropopause near 10 to 12 km reported by Pruchniewicz et al. (76) yield similar mean concentrations (Figure 17a).

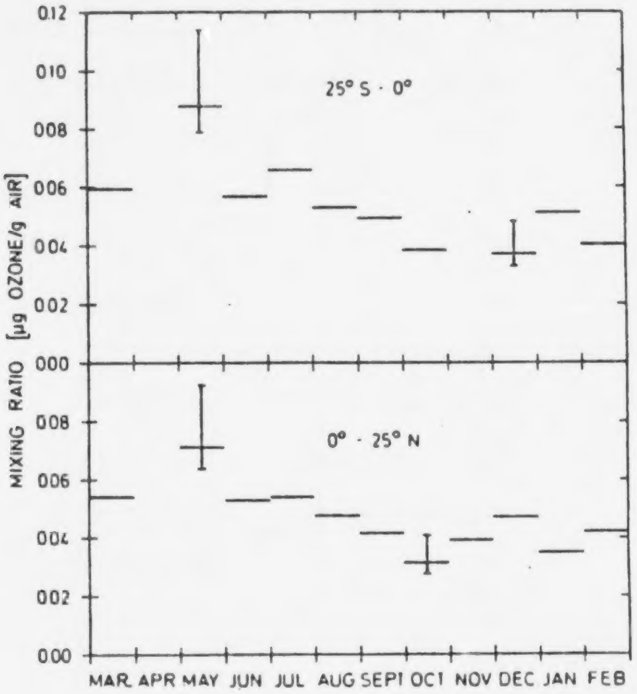


Figure 17a. Mean seasonal variation of tropospheric ozone from airplane measurements for the areas 0° -25°S and 0° -25°N.

Source: Pruchniewicz, P.G., H. Tiefenau, P. Fabian, P. Wilbrandt, and W. Jessen. The Distribution of Tropospheric Ozone from Worldwide Surface and Aircraft Observations. In: Proceedings of the International Conference on Structure, Composition and General Circulation of the Upper and Lower Atmospheres and Possible Anthropogenic Perturbations, Vol. 1. Melbourne, Australia, 1974. pp. 439-451.

From these circumstantial, and heavily smoothed, data it appears that the background level in the lower troposphere of O_3 of stratospheric origin, at times, will reach significant fractions of the Federal 1-hour standard value. It should not be surprising, therefore, if, on occasion, this value would be exceeded. This possibility will be investigated more closely in the subsequent section.

In Table 1 the effects of seasonal adjustments in tropopause height have been estimated to contribute roughly 10 percent to the stratospheric mass budget. These adjustments in tropopause height occur mainly in the transition season and in the jet-stream region of mid-latitudes. It would be difficult, therefore, to separate this effect from the ones already described above. The radioactive fallout distribution discussed earlier already includes this seasonal behavior of the tropopause level which is, to a large extent, caused by the dynamics of jet-stream systems. Therefore, we will not attempt to separate estimates of its contribution to surface O_3 concentrations. Small-scale diffusion near tropopause level is also thought to contribute to the O_3 problem in the lower troposphere only at the noise level.

THE LIFE HISTORY OF STRATOSPHERIC INTRUSION EPISODES

Several case studies of intrusion of stratospheric air into the troposphere have been reported in the literature (9,10,53,70). From these studies the following general pattern emerges.

The "tropopause folding" process injects stratospheric air into the upper part of the frontal zone that is connected to the cyclogenetically active jet-stream system (see Figures 7 and 9). The extent of this stratospheric air intrusion can be delineated very well by potential vorticity

$$P = - g Q_\Theta \cdot \frac{\partial \Theta}{\partial p} \qquad \text{(Eq. 5)}$$

where Q_Θ is the vertical component of absolute vorticity on an isentropic surface (on which potential temperature, Θ, is constant by definition), g is the acceleration due to gravity, $\partial\Theta/\partial p$ is the vertical potential temperature lapse rate in a pressure coordinate system and provides a measure of thermal stability. P is a conservative quantity for adiabatic transport processes. Non-adiabatic processes, which include the effects of radiative warming or cooling of the air mass under consideration and of turbulent mixing with other air masses, render P not conservative.

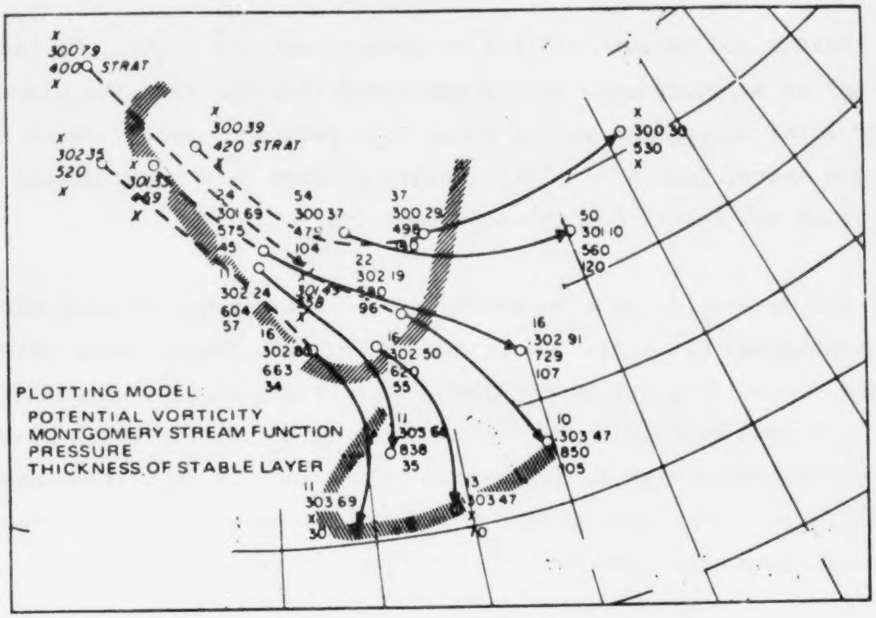
Because of the high stability, $-g \frac{\partial\Theta}{\partial p}$, of stratospheric air, and because of the cyclonic vorticity ($Q_\Theta > 0$) prevailing in the jet-stream region where the stratospheric air intrusions into the troposphere tend to occur, P assumes relatively large values within the intruding air mass (order of magnitude 100 $\times 10^{-9}$ cm sec deg/g). By comparison, the tropospheric air outside these intrusions has typical potential vorticity values of only a few units times 10^{-9} cm sec deg/g. Mixing of stratospheric air with the surrounding tropospheric air will gradually reduce the potential vorticity within the intruding stable air layer.

If this air layer subsiding from the stratosphere is cooled uniformly by radiative heat losses as it descends through the troposphere, its stability, $- g \frac{\partial\Theta}{\partial p}$, should not be affected. We can, therefore, in a first approximation, ascribe decreases of P along an isentropic trajectory of this air mass to the effects of turbulent mixing.

Figure 18 shows a stratospheric air mass intrusion in its final stages as it settles into a "subsidence inversion" above the anticyclonic system behind a cold front. We note the following decreases of P during several 12-hour trajectory segments:

TABLE 4. DECREASE OF P ALONG 12-HOUR TRAJECTORY SEGMENTS

From 16 to 11 $\times 10^{-9}$ cm sec deg/g	= 31% decrease
11 to 11	= 0%
16 to 13	= 19%
22 to 10	= 55%
24 to 16	= 33%
54 to 50	= 7%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50
301 10
560
120
22
302 19
96
11
302 24
604
57
16
302 91
729
107
16
302 80
663
34
16
302 50
620
55
PLOTTING MODEL:
POTENTIAL VORTICITY
MONTGOMERY STREAM FUNCTION
PRESSURE
THICKNESS OF STABLE LAYER
11
305 64
838
35
10
303 47
850
105
11
303 69
30
13
303 47
70

Figure 18. Trajectories on the 300°K isentropic surface. Dashed lines, Nov. 22, 1962, 0000 to 1200 GMT; full lines with arrows, Nov. 22, 1200 GMT, to Nov. 23, 0000 GMT. Values of potential vorticity (units of 10^{-9} cm sec deg/g), of Montgomery stream function (units of 10^7 cm^2/sec^2), of pressure (mb) of the 300°K surface, and of thickness (mb) of the stable layer are entered according to the plotting model; slanting numbers of Nov. 22, 0000 GMT, and vertical numbers for other map times. The centers of the hatched bands mark boundaries on Nov. 22, 1200 GMT, and Nov. 23, 0000 GMT, of stratospheric air from the tropopause level that reaches the ground over the southern United. States.

Source: Reiter, E.R., and J.D. Mahlman. Atmospheric Transport Processes Leading to Radioactive Fallout over the United States in November 1962. In: Radioactive Fallout From Nuclear Weapons Test, Proceedings of 2nd Conference, AEC Symposium Series 5, 1965. pp. 450-463.

Among these widely scattering values a 20 percent decrease of P due to mixing appears to be a reasonably conservative assumption.

An ozone concentration of 80 nanobars at 300 mb, corresponding to 0.44 μg/g, should, therefore, be reduced to approximately 64 nanobars, or 0.35 μg/g, by the time it reaches the lower troposphere in a massive stratospheric air intrusion. This is approximately three times the Federal 1-hour maximum level. For a specific case of radioactive fallout over the southern United

States, Reiter and Mahlman (16,53) estimated that air within the "subsidence inversion" of stratospheric origin was mixed with air from the planetary boundary layer underneath with a ratio of 1 part to 3 parts. With the estimates made above, such mixing still could produce O_3 concentrations somewhat in excess of the 1-hour Federal maximum value.

If one were to attempt an estimate of the frequency of such excessively strong intrusions per year, one is confronted with rather shaky evidence at this time. More detailed investigations, relating perhaps potential vorticity values in a wide range of such intrusions with the intensity of cyclogenetic activity associated with these intrusions, would have to be conducted before one could arrive at probability estimates of exceedence of the Federal standards by stratospheric ozone with some degree of reliability.

If, at this time, we were to ascribe rather arbitrarily a cyclone index of 4.0 as the cut-off value for such massive air intrusions into the troposphere, we can estimate from Figure 10 that perhaps 10 to 12 occasions per year would arise over the United States, in which the Federal 1-hour maximum standard is approached or exceeded. The area covered by such intrusions could be "Texas-sized" (3) in its horizontal dimensions, covering perhaps 1/20 of the United States. We have to realize that the southeastern United States are more prone to be influenced by such stratospheric air mass intrusions than the southwestern or northern tier of states. Realizing this geographic bias in radioactive fallout, hence in stratospheric ozone intrusions, one might cautiously peg the probability of local exceedance of the Federal 1-hour maximum at one case per 1 to 2 years. From different evidence, presented by sporadic ozonesonde observations, Reiter (60) estimated this probability to be 0.2 percent, measured in days of observations on an annual basis at a given location. This estimate agrees well with the one derived above. (Reiter's probability estimate from ozonesonde observations considers only ozone peaks observed in the planetary boundary layer below 750 or 800 mb, depending on location. Carney (35) arrives at higher probability estimates of approximately 11 percent by considering ozone peaks up to the 500-mb level and a "critical" concentration of 0.10 μg/g instead of 0.124 μg/g. Considerable dilution should be expected of ozone peaks observed above the planetary boundary layer during their transit to short distances above the ground.

The conclusion that can be reached so far, therefore, is that ozone concentrations of stratospheric origin observed near the ground can, on occasion, exceed the Federal maximum 1-hour concentration. Such cases, however, are rare and, on the average, far between. They are expected to occur perhaps once a year over the southern and eastern United States.

Careful insentropic trajectory analysis techniques provide a relatively reliable tool to diagnose such events during which ozone of stratospheric origin can reach relatively high concentration levels near the ground (see, for example, 77). Forecasts of such events 24 to 48 hours ahead of time could be made with reasonable reliability. Such forecasts, however, would require computational work of a specialized nature which, most likely, would be considered burdensome by the National Weather Service.

CONFLICTING EVIDENCE FROM DIRECT OZONE MEASUREMENTS

The scientific literature of recent years is full of claims and counterclaims as to the importance of stratospheric air intrusions for ground-level ozone concentrations. We will examine here several of these claims and point out possible sources of errors which might have an effect on the conclusions derived from these measurements. Some of the discrepancies appearing in the published data cannot be resolved easily and will have to await clarification by additional, well-planned and well-executed field experiments.

Measurements of O_3 concentrations on Zugspitze Mountain (3000 m above MSL) Germany, on the one hand, and from Whiteface Mountain (1518 m MSL), New York, and from Hohenpeissenberg (977 m), Germany, on the other hand can be cited as proponents of opposing evidence.

Reiter (34) analyzed daily 1-hour maximum O_3 concentrations observed on Zugspitze and correlated them with the daily mean values of O_3 concentrations.

Figure 19 shows the results of 529 days of data analyzed in this fashion. Federal maximum 1-hour standards were exceeded on 2 days during several consecutive hours comprising one continuing episode (Table 5). (In Figure 19, the limiting Federal standard value is indicated by the hatched line.) Observed maximum exceedance was by more than a factor of two.

The episode of these excessively high O_3 concentrations observed on Zupspitze coincided with a rather anomalous stratospheric circulation pattern (Figure 20) with a pronounced trough over eastern Europe. This trough situation could have produced an enrichment of O_3 in the lower-stratospheric reservoir prior to the tapping of this reservoir by a tropospheric cyclonic disturbance.

The relative infrequency of exceedance of Federal standards on Zugspitze Mountain is in good agreement with our earlier probability estimate of 0.2 percent of local occurrence in mid-latitudes. Nevertheless, the question of instrument inaccuracies at Zugspitze has been raised (Dr. W. Attmannspacher, Director of the German Weather Service Observatory at Hohenpeissenberg; oral communication made at the Dresden Meeting, July 1976) and refuted by recent calibrations (Dr. Reinhold Reiter, Director of the observatories in Garmisch-Partenkirchen and on Zugspitze Mountain; letter communication, 1976). Whereas for reasons of agreement with deductions on expected O_3 concentrations presented earlier in this paper, there should be no quarrel with the Zugspitze measurements, a closer check on the reliability of various measurement techniques may be called for.

Measurements on Whiteface Mountain reveal a frequent exceedance of the Federal standard value for 1-hour maximum concentrations. Even average monthly concentrations approach this value dangerously close (Figure 21), closer than the frequency distribution for Zugspitze shown in Figure 17 would indicate (78). Both the Whiteface Mountain and Zugspitze data indicate relatively high average O_3 concentrations during summer rather than spring. We should keep in mind that during the spring season the stratospheric reservoir shows the highest O_3 concentrations. Figures 17 and 21 would indicate, therefore, at least in a preliminary way, that tropospheric photochemistry and O_3 generation cannot be excluded, not even on Zugspitze mountain.

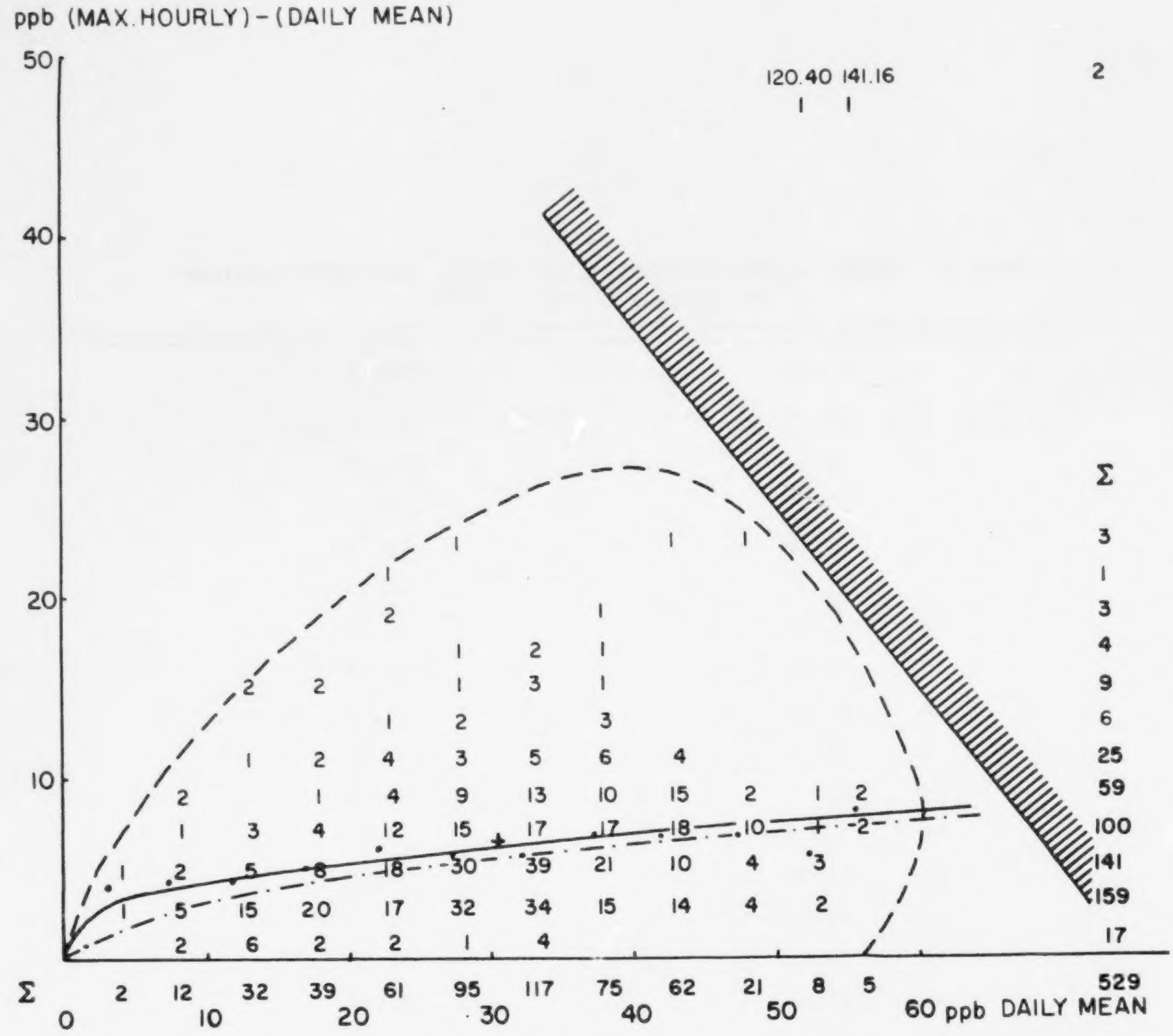

Figure 19. Difference between maximum hourly ozone concentrations (ppb) and daily mean concentrations as a function of daily mean concentrations, observed at Zugspitze (3000 m above MSL) between August 1973 and February 1976. The frequency distribution by 5-ppb classes of the daily mean and 2-ppb classes of hourly maximum minus daily mean is given by the numbers in the diagram. The dashed line indicates the limits of the present data distribution. To the right of the shaded line the federal maximum value of 74.7 ppb would be exceeded. Dots indicate the mean values of (max. hourly - daily mean) in each class of daily mean values. The solid line gives an approximate best fit to these dots. The cross marks the mean value of both distributions, that of (max. hourly - daily mean) and that of the daily mean values. The dashed-dotted line approximates the position of the mode values in each class of daily mean concentrations. Note that two observations fall outside the plotted distribution.

Source: Reiter, E.R. The Role of Stratospheric Import on Tropospheric Ozone Concentrations. Int. Conf. Ox. Poll., Proc. 1:393-410. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

TABLE 5. HOURLY OZONE CONCENTRATIONS (PPB), ZUGSPITZE (GERMANY) ON JANUARY 8 AND 9, 1975

Time	January 8	January 9
1 hr.	25.82 ppb	158.89 ppb
2	27.28	170.36
3	27.94	171.44
4	30.08	159.78
5	31.30	81.33
6	30.93	28.50
7	28.07	25.33
8	27.37	27.79
9	26.91	30.31
10	27.69	30.71
11	37.78	31.43
12	47.88	31.82
13	42.88	32.12
14	50.81	32.22
15	62.21	25.61
16	52.92	25.18
17	52.06	24.88
18	54.83	22.37
19	57.03	22.39
20	62.80	19.84
21	79.85	19.10
22	114.10	17.92
23	157.74	16.89
24	197.55	17.17

Source: Reiter, E.R. The Role of Stratospheric Import on Tropospheric Ozone Concentrations. Int. Conf. Ox. Poll., Proc. 1:393-410. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

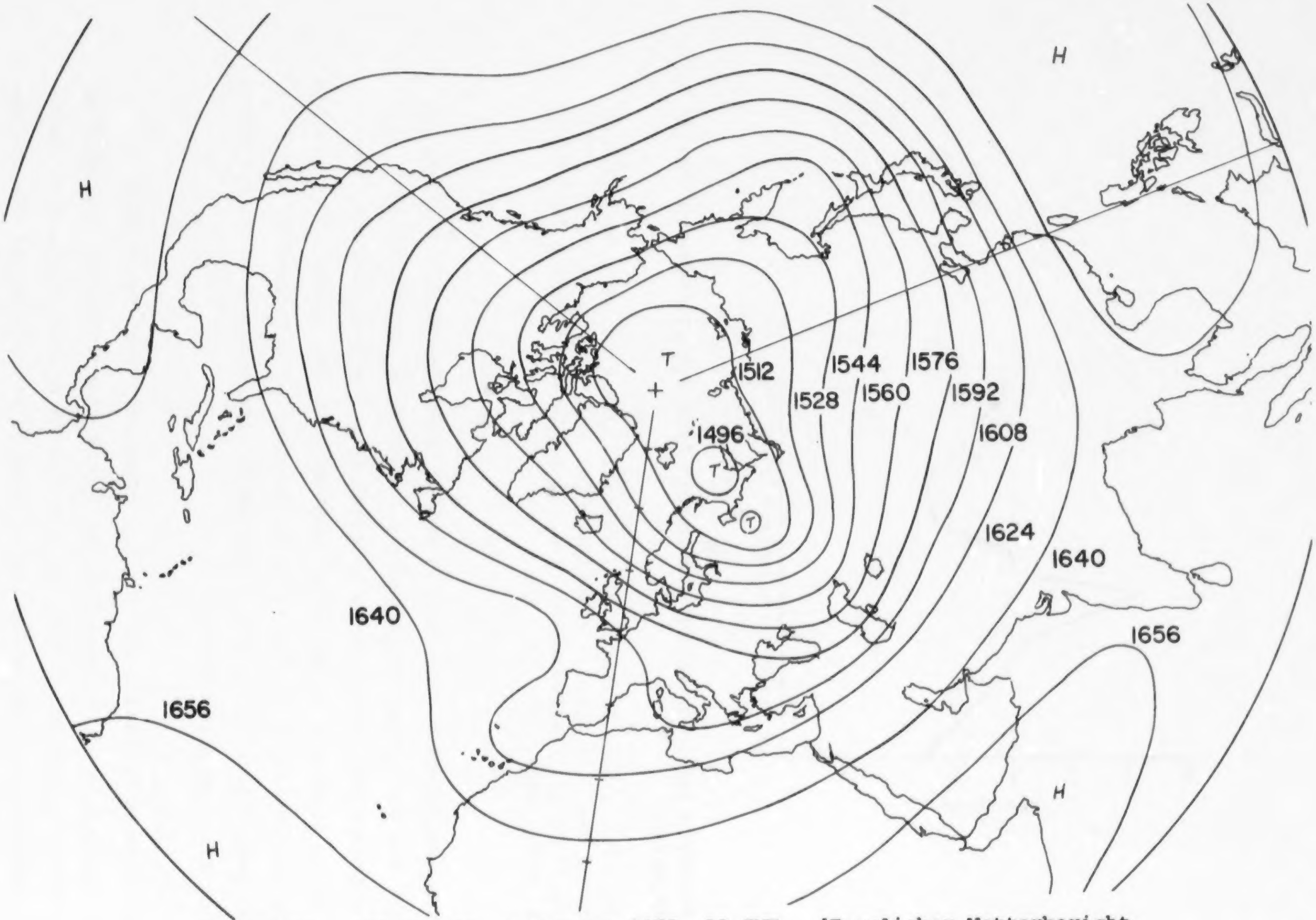
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Figure 20. 100-mb map, 7 January 1975, 00 GMT. [Taeglicher Wetterbericht, Deutscher Wetterdienst, Offenbach.]

Source: Reiter, E.R. The Role of Stratospheric Import on Tropospheric Ozone Concentrations. Int. Conf. Ox. Poll., Proc. 1:393-410. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

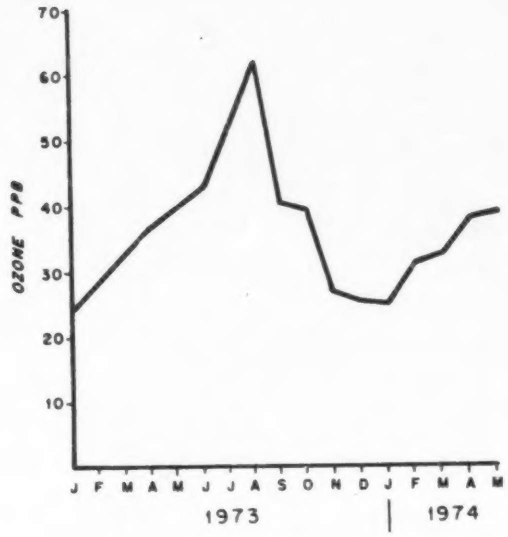


Figure 21. Average monthly ozone concentrations recorded at summit of Mount Whiteface.

Source: Coffey, P.E., W.N. Stasiuk, V.A. Mohnen. Ozone in Rural and Urban Areas of New York State. Int. Conf. Ox. Poll., Proc. 1:89-96. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

The interpretation of Figures 22, 23 and 24 by Coffey et al. (78) is correct: Since the Whiteface Mountain curve of hourly O_3 concentration measurements envelops the other curves obtained from lower elevations, the major source of O_3 should be sought aloft and not near the ground. The earth's surface has to be considered as the major ozone sink, as witnessed by the strong diurnal modulations of O_3 with nighttime minima observed at Pack Forest (Figure 22) and Syracuse (Figure 24).

How, then, can we reconcile our earlier conclusion that ozone from stratospheric sources rarely exceeds Federal 1-hour standards near the earth's surface with Coffey's conclusion that the major ozone source influencing rural areas in the (eastern) U.S. has to be sought aloft? We can present the following arguments.

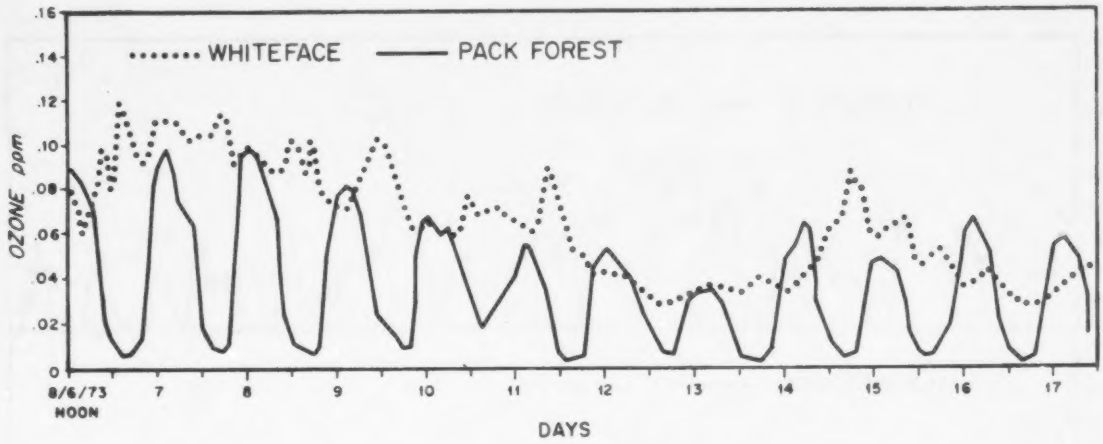


Figure 22. Ozone concentrations at Whiteface and Pack Forest from August 6, 1973 to August 17, 1973.

Source: Coffey, P.E., W.N. Stasiuk, V.A. Mohnen. Ozone in Rural and Urban Areas of New York State. Int. Conf. Ox. Poll., Proc. 1:89-96. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

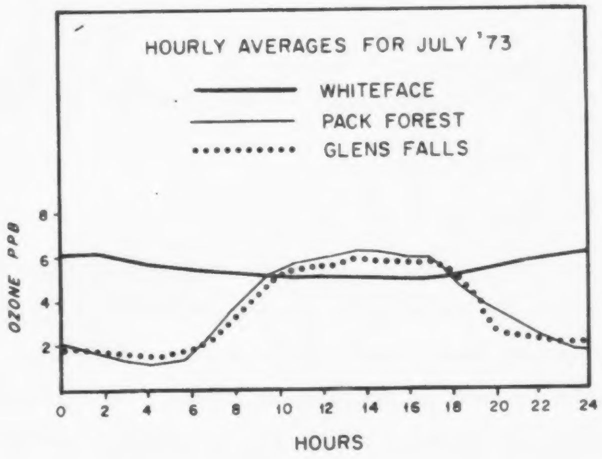


Figure 23. Hourly ozone averages at Whiteface, Pack Forest, and Glens Fall sites for July, 1973.

Source: Coffey, P.E., W.N. Stasiuk, V.A. Mohnen. Ozone in Rural and Urban Areas of New York State. Int. Conf. Ox. Poll., Proc. 1:89-96. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

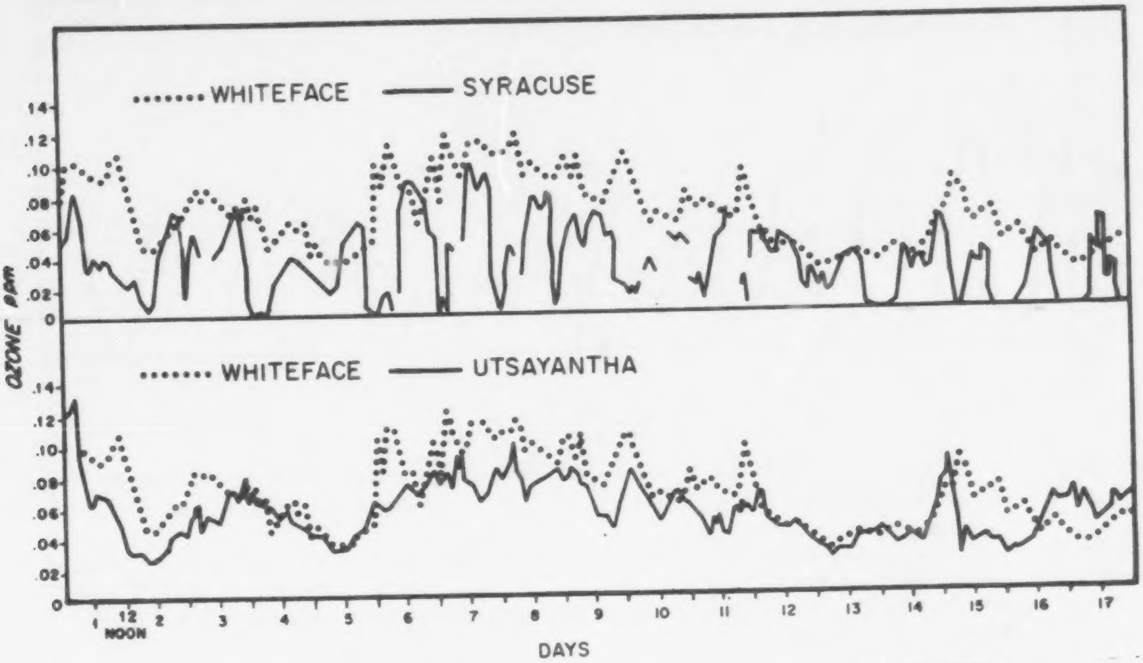


Figure 24. Comparison of ozone concentration at Whiteface site with that at Utsayantha and Syracuse sites for the first 17 days of August, 1973.

Source: Coffey, P.E., W.N. Stasiuk, V.A. Mohnen. Ozone in Rural and Urban Areas of New York State. Int. Conf. Ox. Poll., Proc. 1:89-96. EPA-600/3-77-001a. Environmental Protection Agency, Research Triangle Park, N.C., 1977.

The depth of the mixing layer (ML), as defined by Holzworth (79), and its diurnal variation controls to a large extent the pollution burden of the planetary boundary layer (PBL) (see, for example, reference 80). For the purpose of long-range transport studies we have to acknowledge the fact that, whenever the low-level inversion breaks up, pollutants escape from the PBL and are mixed into a deeper layer of the troposphere. Under most of the anticyclonic conditions, when cloudfree skies permit warming of the PBL during the morning hours and a breakup of the inversion before noon, this additional mixing will not proceed all the way to the tropopause, encompassing the whole depth of the troposphere. If it did, the ascending thermal plumes would result in the development of *cumuli congesti* and of thunderstorms, which are very efficient removers of pollutants. Since such is not the case under most anticyclonic weather patterns, we have to conclude that a second mixing height is reached during the daytime somewhere in the lower to middle troposphere, perhaps between the 1500 and 3000 m levels. (Adiabatic lifting of air by 3000 m with less than 20% relative humidity would not yet produce clouds.) Holzworth's (79) chart of maximum mixing layer heights for July (Figure 25) provides a first guess of the effectiveness of daytime mixing.

Pollution precursors for photochemical ozone generation in the upper part of this mixing layer, which may encompass the lowest 2000 to 3000 m of the troposphere (see, for example, reference 81), will travel long distances relatively undisturbed because they are not in direct contact with the ground.

Little is known at the present about the fate of pollutants in the layer between the nighttime inversion and the daytime maximum mixing height. Ongoing efforts (80) are geared toward determining the transport patterns and diffusion mechanisms controlling the pollutants in this layer.

Measurements made at the Hohenpeissenberg Observatory indicate frequent high O_3 concentrations similar to the ones observed on Whiteface Mountain (Figure 26) (Attmannspacher, oral communication). Occurrence of high O_3 values prior to thunderstorms need not necessarily herald the advent of stratospheric O_3. It could simply mean the advection of O_3 from regions in the upper reaches of the daytime mixing layer that have not yet lost their ozone by contact with the ground. By virtue of the long-range, "undisturbed" transport processes acting in the upper part of the daytime mixing layer, the source of this ozone, or of its precursors, may have to be sought far upstream and many days before its appearance over the measurement site. It appears that Mohnen et al. (26) jumped to conclusions when they tried to link high ozone concentrations in the upper region of the daytime mixing layer to stratospheric air intrusions.

In the light of the foregoing discussion we might accept as real the disagreement between ozone measurements at Zugspitze and at Hohenpeissenberg. Hohenpeissenberg is well within the range of the daytime maximum mixing layer

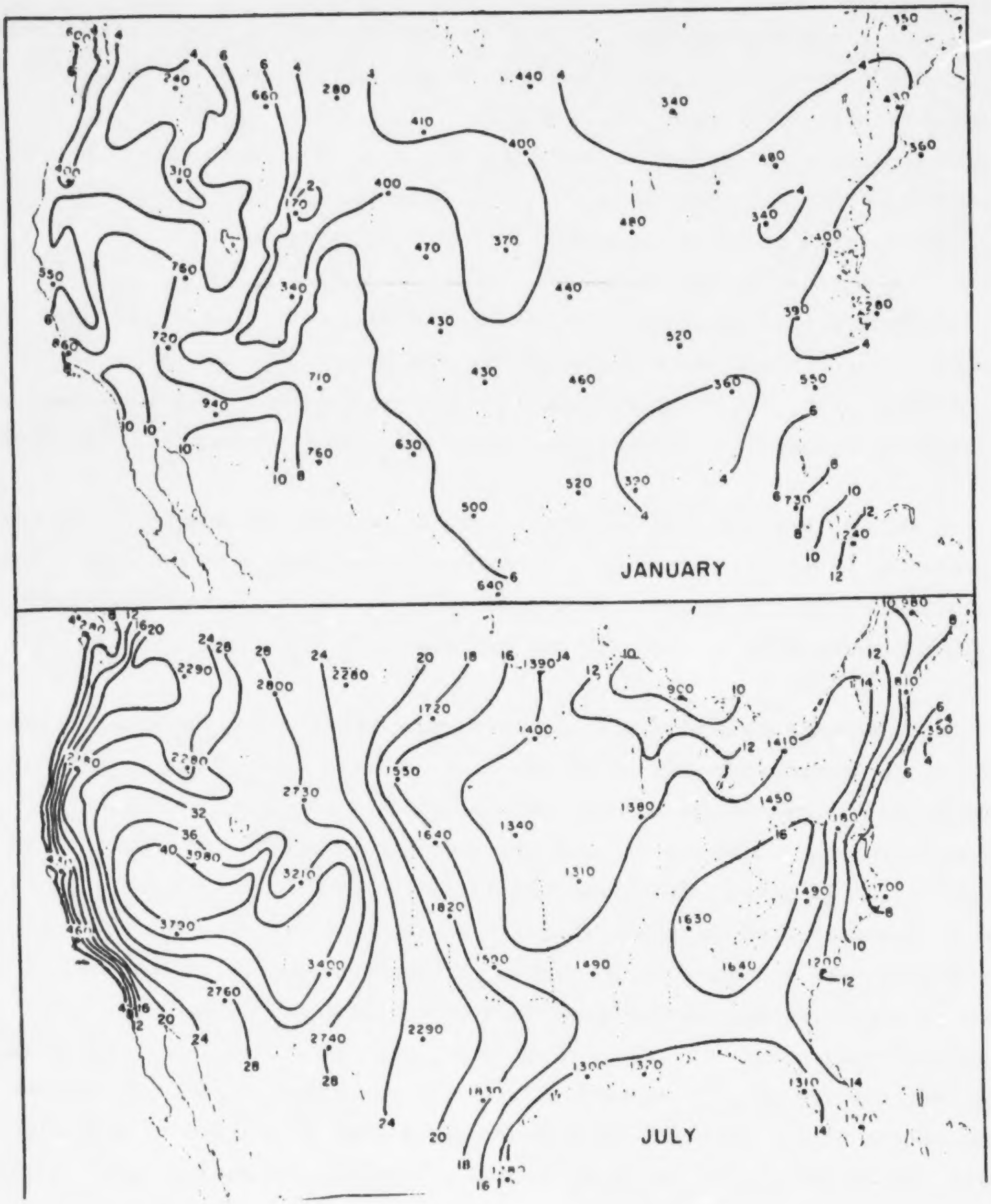


Figure 25. The mean maximum mixing depth for January and July. These data were computed from atmospheric temperature soundings obtained at 45 points in the United States.

Source: Holzworth, G.C. Estimates of Mean Maximum Mixing Depth in the Contiguous United States. Monthly Weather Review, 92(5):235-242, 1964.

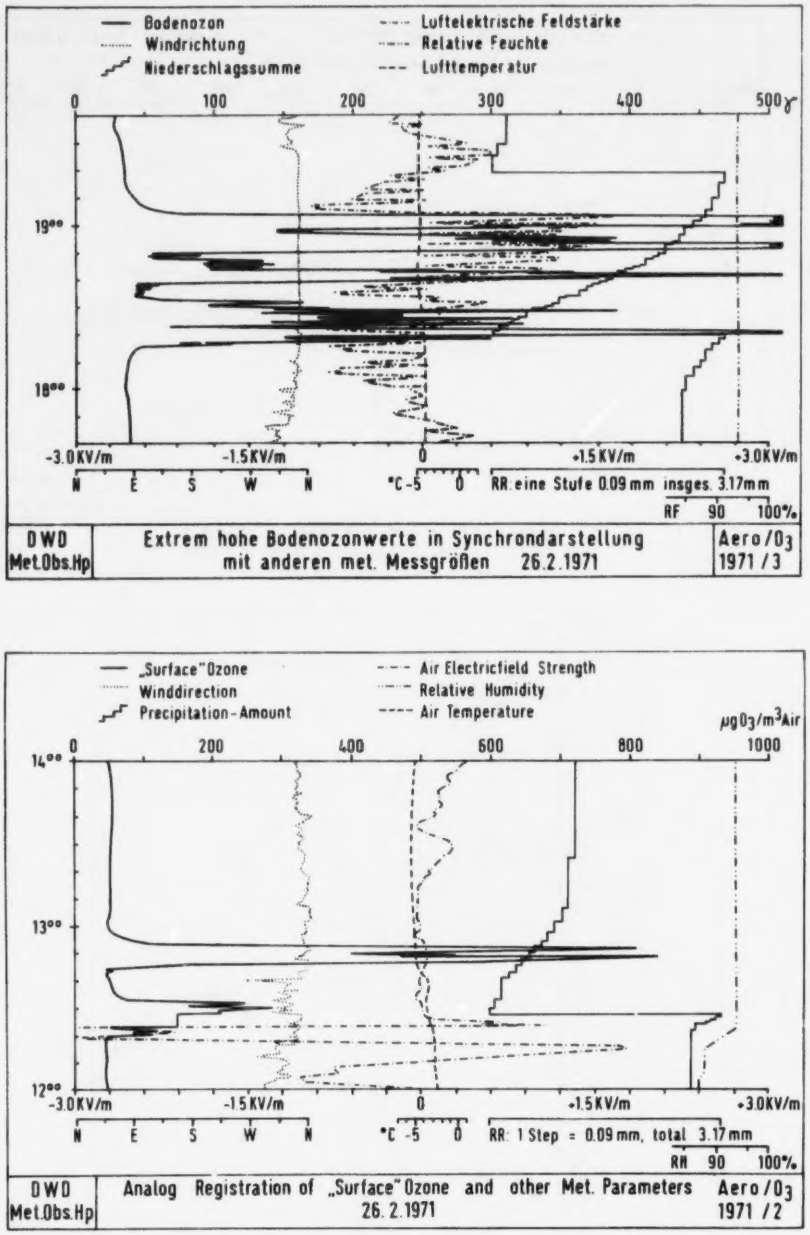
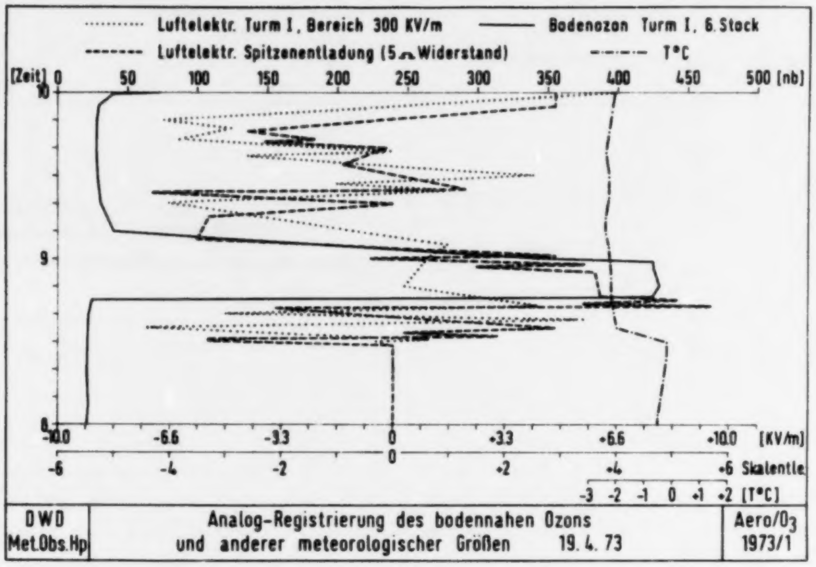


Figure 26. Measurements of ozone and other meteorological problems at Hohenpeissenberg (977 MSL), Germany. Measurements of 23 June 1975 were made under the leading edge of a well developed cumulonimbus. Measurements on 26 February 1971 and 19 April 1973 were associated with strong snow showers and a sequence of cold fronts.

Source: Courtesy of Dr. W. Attmannspacher.



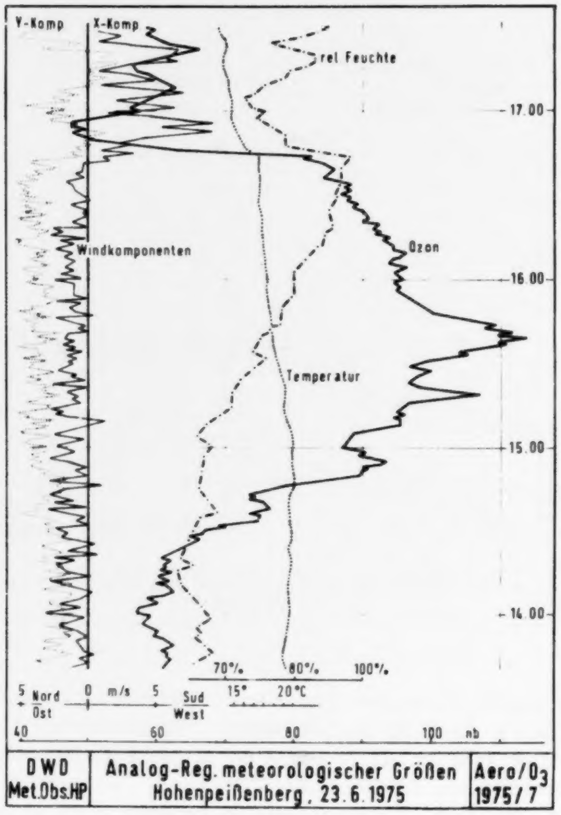


Figure 26. (Continued)

height, whereas Zugspitze Mountain is not, hence the much lower peak ozone concentrations there. Local mountain and valley wind circulation systems are expected to produce some air exchange along the mountain slopes, even up to the 3000-m level. This may be the reason for the appearance of relatively higher O_3 concentrations at Zugspitze in summer and not in spring revealing a similar seasonal trend as on Whiteface Mountain. With such local circulation systems even mountain observatories located as high as the Zugspitze would still be exposed to some tropospherically generated ozone. More research on local circulation systems and on different chemical trace substances is needed to settle this question.

CONCLUSION

In the light of the foregoing discussion, we have to conclude that stratospheric O_3 most of the time only plays a minor *direct* contribution to high ozone concentrations observed in rural regions. The natural background of stratospheric O_3 can be assumed with approximately 15 ppm. On occasion (approximate local probability 0.2 percent of all days), stratospheric O_3 can exceed the Federal 1-hour standard.

Most of the observed O_3 in rural areas appears to come from the upper layers of that region of the lower troposphere that is mixed by thermal convection during daytime hours. Anticyclonic systems are most conducive to carrying high amounts of such ozone of tropospheric (natural or anthropogenic) origin. It will be difficult to separate this tropospherically generated O_3 from the stratospheric contribution, unless other stratospheric and tropospheric trace constituents are examined at the same time.

SUGGESTIONS FOR FUTURE RESEARCH

The numerical estimates of the effects of stratospheric ozone on ground-level ozone concentrations made in the preceding chapters certainly are not without errors. Unfortunately, we are lacking an accurate data base that would allow a more precise formulation of these estimates at this time. The following improvements in our knowledge could be perceived.

(a) From a number of detailed case studies involving isentropic trajectory analysis of stratospheric air intrusions, one should be able to derive a correlation between the intensity of cyclogenetic events in the upper troposphere and the mass of air involved in stratosphere-troposphere exchange processes. These case studies would be rather cumbersome and time-consuming. They are needed, however, to provide a calibration for the statistical assessments of the frequency with which cyclogenetic events of different intensity occur in various sectors of a hemisphere. Airborne measurements, such as those obtained from the NASA Global Atmospheric Sampling Program (GASP) (2) should be used for an assessment of ozone concentrations near the tropopause gap during the incipient stages of stratospheric air intrusions.

(b) The amount of mixing, as a function of time, between air intruding from the stratosphere and surrounding tropospheric air should be established more closely than could be done in the preceding sections. Isentropic analysis of the path of intruding air masses and their potential vorticity budget would offer one avenue of approach. Another, which preferably should proceed simultaneously, would be to probe these stratospheric air intrusions and their tropospheric surroundings by airborne sampling devices for the detailed distribution of trace constitutents of stratospheric or tropospheric origin. Be^7, P^{32}, SO_2, and $SO_4^=$ are constituents which should be prime targets for such investigations. Hydrocarbons and NO_x might also prove helpful in "tagging" certain air masses.

(c) The fate of pollutants in the upper reaches of the layer capped by the maximum mixing height achieved during daytime still is poorly understood. What is their residence time in the atmosphere, allowing for varying synoptic weather conditions and for possible photochemical reactions? Are there effective diffusion mechanisms that spread these pollutants even beyond this maximum mixing height? Detailed case studies can be advocated that involve careful synoptic analyses, and the measurement of vertical profiles of O_3, (see, for example, reference 25), SO_2, NO_x, and hydrocarbons over several locations, distributed over a reasonably large region and over a period of time commensurate to the life history of a distinct air mass.

(d) Even if a stable layer of stratospheric origin impinges upon a mountain range — such as the Alps or the Adirondacks — one will have to exercise great care in interpreting observed trace-constitutent concentrations. The fact that such a stable layer is intercepted by a mountain usually is established from radiosonde ascents, launched at considerable distance from this mountain, and from the temperature record at the mountain observatory. This evidence, however, is remiss in giving us information about the mixing between that stable layer of stratospheric origin and the underlying tropospheric air. Such mixing could be enhanced by local mountain-valley circulation systems as mentioned earlier, and by turbulence generated by the terrain. If an up-slope wind component is observed underneath the stable layer of stratospheric origin, one would have to assume that some of the air of tropospheric origin is forced across the mountain range together with the air in the stable layer, and a certain amount of mixing would be expected between the two air masses. If the tropospheric air were laden with O_3, above-normal O_3 concentrations at the mountain observatory could then be misinterpreted as having come from the stratosphere.

Again, judicious sampling of other trace contaminants, especially of those characteristic for tropospheric sources (e.g., SO_2, $SO_4^=$, and hydrocarbons) would help in establishing the origin, stratospheric or tropospheric, of the observed ozone.

(e) To arrive at a reasonable control strategy of anthropogenic oxidants, one will have to test forecasting schemes which predict the amount of stratospheric O_3 involved in pollution episodes over different regions and at different elevations. The development of such prediction schemes should not stray too far from data sources routinely available from the National Weather Service. One could envision a scheme that uses the correlation between the intensity of cyclogenesis and the amount of stratospheric air injected into the troposphere (see (a) above), the amount of mixing to be expected during the transition of this intruding air mass through the troposphere and the likely course such an intrusion will take ((b) above), and the prognostic charts provided by the U.S. Weather Bureau that give upper-flow configurations and surface frontal systems. One should allow for testing periods during which the predicted progress of stratospheric air intrusions is monitored by airborne and ground-based data sampling.

COMMENTS BY VOLKER MOHNEN

Introduction

Reiter presents a comprehensive assessment of the stratospheric ozone issue. Considering the limited data base available at this time one is more or less forced to rely on circumstantial evidence, estimates, data interpretation, etc. It is, therefore, not surprising to find somewhat differing conclusions drawn by different authors even if the same data basis is used. There are several topics in Reiter's paper that deserve further, more elaborate discussion.

Stratospheric — Tropospheric Transport Processes

Reiter's separation of annual mass flux from stratosphere into

- seasonal adjustment of the tropopause height,
- mean meridional circulation,
- stratospheric exchange between hemispheres,
- large-scale eddies,
- small-scale eddies,

has the inherent danger of "double counting" fluxes. The other alternative would be to treat the exchange process on the basis of only two contributors, namely:

- mean meridional circulation
- eddies (large- and small-scale)

The manner in which the mean and eddy horizontal and vertical ozone fluxes contribute to the total transport has been discussed by London and Park (82,83). London and Park employed the 12-layer General Circulation Model developed by NCAR. The photochemical calculations for ozone have been carried out as time-dependent in a three-dimensional, O-H-N system. Their calculations confirm the dominant importance of large-scale eddy motions in transporting ozone poleward and downward in mid-latitudes. Hadley circulation in the Northern hemisphere is clearly shown in the ozone intrusion through the subtropical tropopause region. However, comparison with observations indicate that the downward branch of the Hadley circulation in the Northern hemisphere as computed by the General Circulation Model is probably too large. This is a result of too strong a return (downward) flow computed by the GCM. The computed ozone flux* is a maximum of 7×10^{10} molecules $cm^{-2} \cdot s^{-1}$ at latitude 60°N decreasing to 3.5×10^{10} $cm^{-2} \cdot s^{-1}$ at the equator. This calculated flux (and its latitudinal variation) compares very favorable with that reported for the Northern hemisphere by

Danielsen (58) (mainly due to large scale eddies)	7×10^{10} molecules $cm^{-2} \cdot s^{-1}$
Nastrom (15) (derived from GASP data, mainly 30° - 60°N)	7.8×10^{10} molecules $cm^{-2} \cdot s^{-1}$
Junge (20) (derived mainly from surface observations)	7.5×10^{10} molecules $cm^{-2} \cdot s^{-1}$

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* Flux determined at the lower boundary, i.e., the earth's surface.

Fabian and Pruchniewicz (16) (derived from surface observation, hemispheric average)	6.6×10^{10} molecules $\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$

Reiter estimates this annual flux to be of the order of 1.44×10^{10} molecules $\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$ (9.215×10^{7} tons ozone/year for the Northern hemisphere (accomplished by Hadley cell circulation only)). Reiter states, "We will have to take into account that the major downward transport during most of the year, accomplished by the mean meridional circulation, occurs in *middle* latitudes and not over the entire hemisphere. An annual flux of ozone of 9.215×10^{7} tons translates into a flux of 2.88×10^{10} molecules $\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$ (or 0.23×10^{-7} $\mathrm{g}\cdot\mathrm{m}^{-2}\cdot\mathrm{s}^{-1}$) if concentrated over half the area of one hemisphere. This number does not yet include the effects of eddy transport processes in the jet-stream region, which also have a preponderance in middle latitudes and on the average, might increase the above estimate by 50%." We can conclude, therefore that Reiter's best estimate yields:

Reiter (34) (estimated from stratospheric-tropospheric mass exchange, Hadley cell circulation, and large-scale eddies)	4.32×10^{10} molecules $\mathrm{cm}^{-2}\cdot\mathrm{s}^{-1}$

Reiter attributes the discrepancy between his ozone flux estimate and the surface ozone fluxes published by others to "anthropogenic contamination of some of the data." However, an equally valid reason for the different flux estimates is the fact that various authors used different ozone mass mixing ratios above the tropopause:

Reiter (34)	$r = 0.5 \times 10^{-6}\ \mathrm{g}\cdot\mathrm{g}^{-1}$
Danielsen (58)	$r = 1.3 \times 10^{-6}\ \mathrm{g}\cdot\mathrm{g}^{-1}$

Reiter states, "0.5×10^{-6} $\mathrm{g}\cdot\mathrm{g}^{-1}$ sets a convenient upper limit of average ozone concentration a short distance above the tropopause." One can argue that during tropopause folding events (large-scale eddies), stratospheric air is intruded from higher levels above the tropopause. Therefore, the mass mixing ratio applicable to these events (latitude >30°N) is $\leq 1.3 \times 10^{-6}$ $g \cdot g^{-1}$ used by Danielsen. For exchange processes at lower latitudes, the intruded air originates from lower levels above the troposphere, hence the 0.5×10^{-6} $g \cdot g^{-1}$ mass mixing ratio is more applicable. In any event, the ozone mass mixing ratio enters critically in any calculation of ozone fluxes. It is mainly for this reason that Danielsen's and Reiter's calculated ozone fluxes differ. It must be reitinerated here, that Reiter's flux estimate is one of the lowest reported in literature.

Mean Vertical Velocities Prevailing in the Troposphere

Reiter calculated a mean vertical velocity of $\bar{w} = 2.74 \times 10^{-3}$ $m \cdot s^{-1}$. December-February data, 10°N to 40°N, at a height of 8 km). At higher latitudes, this value might be different. Other mean vertical velocity calculations range from $(1\text{-}7) \times 10^{-3}$ $m \cdot s^{-1}$ (Lance Bosart, personal communication, 1977) with strong seasonal variation. Average annual values for $\bar{w}$ of 5×10^{-3} $m \cdot s^{-1}$ (15) or 4.7×10^{-3} $m \cdot s^{-1}$ (Danielsen, personal communication, 1977) for mid-latitudes have been used. Following, nevertheless, Reiter's circumstantial evidence, one would arrive at a mean background concentration of ozone for the 10°N-40°N latitude belt of 14.6 $\mu g \cdot m^{-3}$. In a strict sense, this derived mean concentration would be representative only at the 8-km level. Measured annual mean concentrations for this latitude belt and altitude region have been recently shown to be of the order of >40 $\mu g \cdot m^{-3}$ as derived from GASP data (Falconer, personal communication, 1977). This discrepancy cannot be resolved at this time.

Reiter used Junge's (20) estimate for the mean tropospheric residence time of ozone (3.3 months) to arrive at a mean transit velocity of 1.4×10^{-3} $m \cdot s^{-1}$ which then yields, together with Junge's flux value of 0.5×10^{-7} $g \cdot m^{-2} \cdot s^{-1}$, a mean tropospheric ozone concentration of 35.7 $\mu g \cdot m^{-3}$. This is contrary to Junge's (1962) concept of flux derivation. Junge (20) assumed *a priori* (from carefully selected tropospheric background measurement) an annual mean concentration of 50 $\mu g \cdot m^{-3}$, which fixes the annual average for the total tropospheric ozone content to 1.3×10^{8} tons (based on an average tropopause height of 12 km, and an ozone mixing ratio increasing linearly by a factor of two as height increases from 1 km to 12 km). With this basic assumption, Junge eventually arrives at a flux and a mean tropospheric residence time. The concept of estimating ozone background concentration for the entire troposphere from mean vertical velocities is, therefore, at least, debatable.

Zugspitze Mountain Measurements

Reiter states "The mode value of observations appears to lie close to one-half of the Federal 1-hour standard value. Allowing for additional dilution between 3000 m and the general terrain level of the eastern United States, the estimates of $0.05 \times 10^{-6}\ g \cdot g^{-1}$ of 24-hour averages maximum ozone concentrations made above appear to be reasonable. Aircraft measurements below the tropopause near 10 to 12 km reported by Pruchniewicz et al. (76) yield similar mean concentrations." This circumstantial evidence is acceptable for ground-level concentrations (measurements in the Adirondacks, Whiteface Mtn., N.Y., and Olympic Mountains, Washington; see Coffey et al. (24), Chatfield et al. (23)), but debatable for upper tropospheric concentrations: Pruchniewicz et al. aircraft data are only reported for 25°N - 0° and 0° - 25°S. It is well known that the tropospheric ozone concentration is lower in low latitudes, i.e., from 30°N to 30°S. GASP measurements at mid-latitudes show higher values (15).

The Troposphere as a Source or Sink for Ozone

Reiter raises at several occasions the issue of "ozone of tropospheric (natural or anthropogenic) origin." The existence of photochemical ozone episodes around major metropolitan complexes is well established. The geographic extent of these regions of high ozone concentrations is not yet established. It is therefore conceivable that rural or remote locations can suffer from elevated ozone concentration as a result of "long-range transport of ozone and/or ozone precursor gases." Furthermore, the question of tropospheric ozone production and destruction from natural precursor gases has not been resolved yet. Two opposite views are presented by, for example, Chameides and Stedman (84), and Fishman and Crutzen (85). Chameides and Stedman find: "It is interesting that as we now understand the tropospheric ozone budget, the major role of photochemistry in the ambient atmosphere, where nitrogen oxide densities are low, is to act as a net sink for ozone. Thus the calculated ozone abundance with photochemistry and transport is *lower* than the abundance calculated with transport alone." On the other hand, Fishman and Crutzen's numerical investigations show that "it becomes difficult to explain the observed tropospheric ozone profiles. We suspect, therefore, that catalytic ozone-*producing* mechanisms are operative in the troposphere in addition to those we have considered in this study." It is obvious that better information of the tropospheric $NO-NO_2$ concentration and on critical rate constants (e.g., for $NO + HO_2$) is required before this controversy can be resolved.

Therefore, the origin of ozone observed at rural-remote stations still remains open to debate. Reiter's circumstantial evidence for a low-tropospheric "ozone climatology" can, therefore, not be disputed on the basis of existing data.

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